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CHEMICAL CHARACTERISTICS OF ORGANIC COLOR IN WATER

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27 Abstract

The colloid charge titration technique described by Kawamura and Tanaka, was used to measure the charge on color-aluminum, color-thorium, and color-lanthanum dispersions. This method was able to measure the charge on colloids which were too small to be seen, thus replacing the Briggs microelectrophoresis cell technique. Tests were conducted using a Lumetron Model 402E filter photometer to obtain data points of pH vs % transmission; and pH vs total organic carbon. A computer program was designed to perform a least squares analysis on all the data points to determine the shape of the curve, and the curves were then plotted on a plotter. The program which was developed will analyze as many as 15 sets of data. Analyses made on data taken from actual colored influent will provide operators with plots which show the optimum operating conditions for a particular color removal problem. (Lowry-Texas)

(WRSIC abstract)

Abstractor Mark V. Lowry | Institution Texas Univ, Austin

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INTRODUCTION

This final report covers research not described in earlier publications (1, 2, 3) concerned with determination of organic chemical structures of degradation products and molecular size distribution of natural color producing substances.

The work reported herein has been directed at broadening our understanding of the mechanisms involved in the coagulation of natural color systems with certain metallic salts. Although the process has been practiced for many years and studied extensively within the last decade, fundamental questions remain unanswered regarding the role of electrostatic charge reduction and the generally beneficial effect of the calcium ion during coagulation. Earlier work by Black and his co-workers (4, 5, 6) using microelectrophoretic techniques led to the conclusion that minimization of the negative surface charge on color macromolecules was prerequisite to good color coagulation. Initially these findings seemed to support the colloid destabilization theory of color removal (double layer compression) first proposed by Saville in 1917. Later work by Black, et al. (7), Hall and Packham (8) and Maulding and Harris (9) pointed out several inconsistencies with existing coagulation data and this physical theory, and provided stoichiometric data on coagulant-color interactions suggestive of a chemical reaction type mechanism. Although the favor of each of these extreme theories has waxed and waned the only charge measurements involved have been obtained via microscopic examination of floc particles in a Briggs microelectrophoresis cell. There are disadvantages to this charge measurement procedure: Uncoagulated color samples contain color macromolecules which are too small to be seen and coagulated particles must grow in size sufficiently to become

visible before charge measurements can be obtained. Thus, potentially, the critical time period of charge change is missed. Clearly an independent charge measurement is needed to verify or reject earlier findings and preferably it should not be susceptible to particle size.

In this study, charge measurements on color-aluminum, color-thorium, and color-lanthanum dispersions were obtained using the colloid charge titration technique described by Senju (10) and more recently by Kawamura and Tanaka (11). This procedure obviates the disadvantages of the electrophoretic technique. In addition, the effects of calcium and magnesium on the charge relationships were investigated.

EXPERIMENTAL RESULTS

1. ALUMINUM

The natural surface charge of untreated color producing macromolecules is substantially negative over the pH range of interest in natural waters (figure 38). Increasing pH results in increased negative charges and similar behavior was observed for each of the three waters used in this study. Furthermore, these observations are identical with those reported by Kawamura (12) for the colored waters of the Olentangy River.

The effects of aluminum sulfate in the surface charge and degree of removal of natural color is shown in figures 1 through 6. The optimum pH for good removal is symmetrically centered around pH 5 and is relatively insensitive to alum dose except at very high values of coagulant dosage. The width of the pH zone of good coagulation (greater than raw water %T of 60) increases in a linear fashion with coagulant dosage (figure 7). It is obvious from an inspection of figures 1-6 that coagulation does not occur solely at zero charge, indeed optimum coagulation occurs in all cases at substantially negative values of surface charge. In the high alum dosage (150 ppm) case optimum removal correlated with maximum negative particle charge whereas at reduced coagulant dosages (100 and 60 ppm) the correlation was with negative charges between the maximum and minimum values. Correlation of optimum coagulation conditions with zero or even minimum negative charge was not observed in any combination of variables.

This data is inconsistent with results predicted with the double layer compression theory. Compression of the Helmholtz double layer

would demand a correlation of zero charge with optimum removal but can offer no explanation for charge reversals of the type displayed in the alum 60 and 100 curves (figures 3 and 5). This point has been discussed by Singley (13) in reference to microelectrophoretic charge measurements. With the latter technique most workers have found extensive negative to positive charge reversals at higher aluminum concentrations. The colloid titration method, employed in this study, showed more substantial reversals at 60 and 100 ppm alum than at 150 ppm alum. The important point remains, however, that in the absence of charge correlation it is clear that some other mechanism is operative and that all charge effects are coincidental.

Figure 39 is an equilibrium stability diagram for an aqueous aluminum system at 25°C. The solid lines indicate the concentrations of various hydrolysis products of aluminum (III) in equilibrium with $Al(OH)_3$ (s) at any pH. Calculations used in the construction of this diagram are presented in Appendix I. Although there is no certainty that the coagulating systems investigated in this study were in true chemical equilibrium it is interesting to note that the region pertinent to the study conditions (i.e., -logC 3 to 4 and pH 5) lies completely outside the zone of stable $Al(OH)_3$ (s). If the coagulation mechanism involved a simple enmeshment of color macromolecules within a settleable $Al(OH)_3$ floc matrix one might expect the optimum pH for coagulation to coincide with that of greatest Al insolubility (approximately pH 6.5 or greater). Since this is not observed it is attractive to <u>assume the involvement</u> of specific chemical interactions between color macromolecules and one or more hydrolysis products such as $Al_{13}(OH)_{34}^{+5}$ and $Al_7(OH)_{17}^{+4}$, the two most stable forms at pH 5 shown in the stability

diagram. The speculative nature of these statements must be emphasized, as the chemical natures of aluminum hydrolytic products and of the organic functional groups present in color are largely unknown. The chemical interactions involved could be simple in nature leading to insoluble "aluminum-color" precipitates or more probably could be one step in more complex multiphase reactions in which chemi-sorption is involved. Stumm and O'Melia (14) have developed an adsorption model for coagulation which is influenced by coagulant concentration, pH and surface area of the dispersed phase. Whereas the data obtained in this study is totally inconsistent with the double layer compression and $Al(OH)_3$ enmeshment theories, it is not inconsistent with an adsorption model which includes specific chemical interactions.

The data in figures 8 through 11 show the effect of added calcium ion on the coagulation parameters with an alum concentration of 80 ppm. At low calcium concentrations (18 and 37 ppm) the optimum pH remains centered at pH 5 although broadening of the pH zone is significant at calcium values of 100 and 150 ppm. Data obtained with alum concentrations of 60 ppm indicate that large calcium values slightly increase the degree of color removal although the principal effect of Ca^{++} is the broadening of the pH zone of good coagulation (figure 7). The criterion for "good coagulation" is, as before, percent transmission values greater than the natural untreated water (60%T). The slight decrease in width of the zone at very low Ca^{++} values is unexplained but reproducible. The same low Ca^{++} values caused optimum coagulation with 80 ppm alum to correlate with maximum negative charges. In the absence of calcium ion, this occurred only with high alum concentrations.

Small concentrations of Mg^{++} tend to decrease the pH of optimum coagulation with alum from pH 5 to approximately pH 4.0 and to increase the negative value of the particle charges (figures 12 through 15). When calcium and magnesium are present together the effects on optimum pH, width of coagulation zone and degree of removal are identical to the calcium alone effects. However, the particle charges measured under these conditions were the lowest obtained in the entire alum sequence (figures 16 through 19).

2. LANTHANUM

In figures 20 through 25 it can be seen that the optimum pH for coagulation of color with lanthanum salts is a function of lanthanum dosage. This is contrary to the behavior of aluminum salts although the degree of color removal is not as great with lanthanum as it is with either aluminum or thorium. Low dosages of lanthanum (less than 80 ppm) operate best at around pH 5.8 and higher dosages approach an optimum pH of 7.0. The width of the coagulation zone is a function of coagulant dosage as shown in figure 7. No correlation exists with particle charge and extent of removal, and calcium ion has little effect on either particle charge or degree of removal although the width of the coagulation zone is extended significantly to the acid side by 36 ppm Ca^{++}. As in the case with aluminum, the study conditions define a point on the lanthanum stability diagram (figure 40) which is completely outside the stable zone of solid lanthanum hydroxide.

3. THORIUM

In terms of carbon removal, color removal and increase in percent transmission, thorium salts are preferable to either aluminum or

lanthanum as shown in figures 28 through 33. The optimum pH is a function of dosage, as was observed with lanthanum, although the entire zone of coagulation with thorium lies substantially to the acid side (pH 3 to 5.5). The width of the zone is a function of thorium dosage (figure 7). In the absence of calcium ion no correlation exists between particle charge and extent of color removal. Small concentrations of calcium (18 ppm) actually reverse the particle charge from negative to positive (figure 34) although higher calcium concentrations result in extremely negative charge values (figures 35 through 37). In any case no correlation exists between particle charge and extent of removal and as with the other metal coagulants, calcium concentrations tend to broaden the width of the good coagulation zone, although the system point for best coagulation lies outside the zone of stable thorium hydroxide (figure 41).

EXPERIMENTAL PROCEDURES

1. SOURCE OF COLORED WATER

The colored water used in this study was obtained from a natural swamp near Pilchuck Creek, draining Lake Cavanaugh in northwestern Washington. The swamp surface area is approximately 20,000 ft^2 and has an average depth of 10 feet. Samples were collected in five gallon polyethylene containers, transported to the laboratory and stored at 5°C until use. The water contained no natural turbidity and thus roughing filtration was unnecessary.

2. ACIDITY MEASUREMENTS

All pH values in this study were obtained with a temperature compensated Beckman Model Zeromatic II pH meter equiped with glass and calomel electrodes.

3. ABSORPTION MEASUREMENTS

All percent transmission values were obtained with a Lumetron Model 402E filter photometer equipped with 2 cm cells and glass filters having maximum transmission at the indicated wavelength.

4. COLOR

A standard curve (Figure 42) was employed which permitted the conversion of color values at any pH to color values at pH 8.3. The curve was generated by measuring the pH, % T at 420 mμ and color values of a series of platinum-cobalt standards prepared as described in Standard Methods. To use this conversion curve it is first necessary to obtain a color value at the pH of the sample in the ordinary way, i.e., by use of a % T at 420 mμ vs. standard color value curve as

outlined in Standard Methods. This curve is displayed as the right hand section on the conversion chart. Once the color value at any pH is known, the color at pH 8.3 can be rapidly estimated by drawing a straight line through the color value (right hand axis) and the sample pH.

5. ORGANIC CARBON MEASUREMENTS

The details of the non-dispersive infrared procedure used in this study for organic carbon measurement have been reported by Emery, Welch and Christman (15). Standard solutions of $NaHCO_3$ and Na_2CO_3 (1000 mg/l each) were prepared bi-weekly and stored at 5°C. An operational flow diagram is shown below.

Sample —inject→ Total Carbon (TC)

Sample —acidify, sparge with N_2→ —inject→ Apparent Total Organic Carbon (AOC)

Distilled Water —acidify, sparge with N_2→ —inject→ Acid Blank (AB)

TOTAL ORGANIC CARBON (TOC) = (AOC) - (AB)

TOTAL INORGANIC CARBON (TIC) = (TC) - (TOC)

6. JAR TESTS

The general jar test procedures employed in this study were similar to those described by Black and his co-workers (4, 5, 6). A Phipps and Bird multiple stirrer equipped with constant level siphons for sample withdrawal was used and pH adjustments were made with calculated additions of HCl, HNO_3 or NaOH prior to the addition of coagulant. Stock solutions of the following reagents were maintained:

$Al_2(SO_4)_3$	10 mg/ml	as aluminum sulfate
$La(NO_3)_3$	"	as lanthanum nitrate
$Th(NO_3)_3$	"	as thorium nitrate
$CaCl_2$	"	as calcium chloride
$MgCl_2$	"	as magnesium chloride

Parameters monitored on coagulated samples included percent transmission at 420 mμ, residual organic carbon, residual Ca^{++} and Mg^{++}, and total colloid charge in meq/l.

7. IRON DETERMINATION

Iron was determined according to the ortho-phenanthroline procedure outlined in Standard Methods. Absorption measurements were made at 510 mμ with a Perkin-Elmer spectrophotometer.

8. COLLOID TITRATION

The basic technique of the colloid titration has been described in a series of articles by Kawamura and Hanna (Water & Sewage Works, Sept. 1966) and in a book by Senjue (in Japanese), Principles of Colloid Titration. Generally, negatively charged colloital particles (or macromolecular particles) such as those responsible for organic color, may be quantitatively titrated by adding an excess of the positively charged colloid, glycol chitosan (GC). Excess GC is back titrated with a standard negative colloid, polyvinyl alcohol sulfate (PVSK) using Toluidine Blue as an internal indicator.

The following reagents were maintained:

a. Polyvinyl Sulfuric Acid Potassium Salt (PVSK)

0.005 N solution
equivalent weight 162.2 gm/eq
% esterification 96.1 (dependent on batch)

b. Methyl Glycol Chitosan (MGC)

0.005 N solution
molecular weight 375.2 gms, difficult to dissolve

c. Toluidine Blue 0 (TBO)

0.1% aqueous solution
samples were tried from different supplies (City Chemical, Kodak and Wako) and Kodak TBO was the most satisfactory

The end point of titration was determined as a formation of visual microflocs instead of color change. As noted in the book by Senju (Colloid Titration) the formation of flocs or precipitates follows instantaneously after the reaction of PVSK with TBO. This method of determining the end point was accepted because of the very vague change in color from blue to pink. It should not affect the validity of the Colloid Titration method since the charge is calculated from the difference between the sample titration and blank titration, both of which are carried out in the same manner.

Initially the concentration of MGC and PVSK was fixed at 0.001-N as recommended by Kawamura, however the determination of the end point by the observation of color change was beyond the visual abilities of the titrators. The concentration of both reagents was increased five times, and the volume of MGC to be added before titration was increased to 10 ml. The results were far better than in the previous experiments. Alternatively, the volume of MGC can be half as much as that used in these experiments (10 ml to 5.0 ml), and titration performed with 0.0025-N PVSK, to reduce the consumption of MGC, which is rather expensive.

It is advisable that the sample to be used for the jar tests should not be used for the colloid titration, since the length of time involved may lead to aging effects on the floc particles. The

following sequence of additions was developed to minimize the time between reagent addition and charge determination.

For the preparation of 30 samples:

Time required: 20-30 minutes steps 1-5
45-60 minutes step 6

1. Rapidly mix one liter of colored water sample (or distilled water for blank) with coagulation reagents.
2. Add 20 ml of desired stock cation solution to each sample with an automatic pipet.
3. Adjust pH of sample to desired level, by addition of predetermined volumes of standard HCl, HNO_3 or NaOH.
4. Add 3 drops of TBO to each beaker.
5. Add 10 ml MGC to each beaker with an automatic pipet.
6. Titrate each sample with PVSK recording volume of PVSK and pH. Titrate in semi-dark room with Tensor light behind beaker. Samples must be constantly and gently stirred during titration.

Charge Calculation

Sample size:	20 ml	Blank size:	20 ml
HCl or NaOH:	1.0 ml	HCl or NaOH:	1.0 ml
MGC:	10 ml	MGC:	10 ml
PVSK:	P ml	PVSK:	P' ml

Charge = (P-P') x (1/200) eq/l x 1000/sample volume

9. COMPUTER PROGRAMS FOR CURVE FITTING (APPENDIX II)

Colloid Titration

The program will give the best fit curves for pH vs. PVSK requirements and pH vs. colloid charge with plotting outputs. The

program was made for this particular experiment considering the easiness of finding the mistakes when used by other than the programmer. The variables are named in such a way as to distinguish each of the input data and calculation processes in the program.

Basically the program will calculate the coefficients for the polynomials best fit for the set of input data by the Least Square Method. It will calculate the coefficients for the sample titration first, then for the blank titration. The input data for each of the titrations is limited to 50 values of pH and PVSK but they can be increased by changing the DIMENSION statement. To fully understand the program the user must have a background in the LEAST SQUARE Method as well as the method of solving simultaneous equations.

The program consists of two main parts, the main program and the subprogram INVR. INVR is made by the University of Washington as a package program for the solution of simultaneous equations. The main program will supply the necessary data for the subprogram by creating the matrices to be solved. Also it will give two plotouts of the resultant polynomials for the sample and the blank titrations and for the charge calculated from the difference between the two.

The cards to be changed or renewed every time the program is run are the following:

Statement Number

4. Starts from the 7th column, II = ?

6. Starts from the 7th column, M = ?

Data cards

1. Data identification card (The first card of the data deck)

2. Data for Sample titration with a blue card at the end

3. Data for Blank titration with a red card at the end

Statement No. 4 in the main program is to designate the number of sets of data (one set of data means, the data identification card, sample titration data cards, with a blank card in the end, blank titration data cards with a blank card in the end. For example, if you have three sets of data to be processed at the same time, statement no. 4 card should look as follows:

```
      1 2 3 4 5 6 7 8 9 10 11 12 13.....column no.
                  I I  =    3
or                I I = 3
```

Statement No. 6 in the main program is to designate the order of the polynomial to be used for the approximation of the titration curve. The manner in which the variable is to be punched is the same as for statement no. 4. It should look as follows:

```
      7.......
      M = 6
```

The order of the polynomials should be great enough to follow the trend of titration smoothly and precisely, but small enough to eliminate the over sensitivity to the extraneous values. From a program made to determine the order of the polynomial, the 6th or 7th order turned out to be the best for colloid titration curve fitting.

Data cards should be punched as follows:

1. Data identification card

   a) from column 1 to 70

      Date of sampling, Date of experiment and Coagulant used

The same is true for both sample and blank titration data. After punching 10 data cards a blank (non punched) card should follow. Therefore the whole set of data deck would look like:

card

1.....data identification card
2 - 11.....sample titration data
12.....blank card
13 - 22....blank titration data
23.....blank card

If more than one set of data is involved, the identification card of the next set of data should follow the last card (blank card) of the previous set of data. The last data deck should be followed by the EOF card.

PROGRAM COLLOID

Statement Number	Function
4	Number of sets of data to be fed into the program.
6	The order of the polynomial used in the curve fitting operation.
9	Volume of sample titrated.
71	pH minimum value on the graph - sets the lower value for the pH scale.
72	pH maximum value on the graph.
73	Sets the minimum value for PVSK to be graphed. The value for start is taken from column 71-80 on the data identification card.
74	The 3.0 controls the scale of the PVSK on the graph. Only those values within 3.0 ml of the starting volume will be included.
75	Sets the minimum values on the charge vs. pH graph.
76	Sets the maximum value on the charge vs. pH graph.
96	Calculates the charge for 201 points across the graph.

Jar Test

The program will give the best fit curves for pH vs. %T and pH vs. TOC with plotting outputs. It is good for this particular research but not for general use.

The program will calculate the coefficients for the polynomials best fit for the set of input data by the Least Square Method. The maximum sets of data (one set means pH, %T, TOC, EDTA for Total Hardness, EDTA for Ca^{++} at one particular pH) for this program is 15.

The program consists of two main parts, the main program and two subprograms, GEBS and INTR. INVR used in the program for the colloid titration may replace the two subprograms, GEBS and INTR, however it was the programmer's intention to try a different method.

The time limit of the program should be also less than 50 seconds even with more than 10 sets of data (one set means one run of experiments). The core space requirements are the maximum available in CDC 6400, because there are a number of dimensioned variables. There are two cards inserted in the main program which has to be changed every time a different number of data is to be processed (statements no. 6 and 56).

The cards to be changed or renewed every time the program is run are the following:

Statements

6. Starts from the 7th column, II = ?

56. Starts from the 7th column, M = ?

Data cards

1. Data identification card (The first card of the data deck)

2. Data for pH

3. Data for ZT

4. Total Carbon Data

5. Data for EDTA requirements for T. Hardness

6. Data for EDTA requirements for Ca^{++}

The first card in the main program to be changed is the same as the one in the program COLLOID. The number indicates the number of sets of data to be processed. The number has to be in integer form. The same applies to the second card which is to identify the order of polynomial to be used. It again can be either 6 or 7, but if it is 5, a slight deviation occurs. In this particular program, the programmer assumed percent transmittance and TOC to be the same as those of the original raw water at pH's 0.5, 1.0, and 11.0, 12.0. The reason for this is to smooth out the curve at either end of pH. Therefore when the plotouts are to be interpreted caution has to be taken not to attach any significance to the values on either end. (The valid range of pH should be the one of the original data.)

Data cards should be punched as follows:

1. Data identification card

   a) from column 1 to 10
      Date of Experiment
   b) from column 11 to 20
      Date of Sampling
   c) from column 21 to 30
      Coagulant used
   d) from column 31 to 40
      Concentration of coagulant used in mg/l
   e) from column 41 to 50
      Sample volume for EDTA titration

f) from column 51 to 60
EDTA dilution factor
(If 1/5 of the original concentration was used, the dilution factor would be 5.0)

g) from column 61 to 70
EDTA factor

h) from column 71 to 72
Number of sets of data points

i) from column 73 to 80
The starting pH on the plotout.
(If pH starts from 0.0 on the plotout, the maximum shown will be 10.0, and if pH starts from 2.0 the maximum will be 12.0.)

2. Data cards

All the data should be punched in F6.3 Format. This means there are three digits below the decimal point and two above it. The total field length for one number is 6 including the decimal point. See the example in the following page.

If the following data were given to be punched,

pH	%T	TOC	T.H.	Ca
3.10	73.20	22.00	3.80	1.20
4.00	78.70	19.00	4.65	1.80
4.40	77.30	18.00	2.40	1.50
5.00	79.30	17.00	3.15	1.55
.	.	.	.	.
.	.	.	.	.
.	.	.	.	.

the first card should look as:

```
column..12345678901234567890123456789012345678901234567890
data.... 3.10  4.00  4.40  5.00  ......
```

the second card:

73.20 78.70 77.30 79.30 .....

the third card:

22.00 19.00 18.00 17.00 .....

the fourth:

3.80 4.65 2.40 3.15 .....

the fifth:

1.20 1.80 1.50 1.55 .....

If more than one set of data is involved, the identification card of the next set of data should follow immediately after the last card of the previous set of data (the last card should be Ca^{++} EDTA titration data card).

JAR TEST

Statement Number	Function
6	The number of sets of data to be handled.
56	Determines the order of polynomial used in the curve fitting operation.
92	The starting pH value for the pH scale. This value comes from column 73-80 of the data identification card.
93	Sets the pH scale on the graph at 10 pH units above the starting value.
94	Sets the minimum %T value on the graph.
95	Sets the maximum %T value on the graph.

APPENDIX I

CALCULATIONS FOR THE ALUMINUM STABILITY DIAGRAM

$$Al^{+3} + H_2O = Al\,OH^{+2} + H^+ \qquad K_1 = 10^{-5.0}$$

$$Al^{+3} + 3H_2O = Al(OH)_3(S) + 3H^+ \qquad K_2 = 10^{-9.5}$$

$$Al^{+3} = \frac{(H^+)^3}{10^{-9.5}}$$

---

at pH 2 $\quad Al^{+3} = \dfrac{10^{-6}}{10^{-9.5}} = 10^{+3.5}$

pH 4 $\quad Al^{+3} = \dfrac{10^{-12}}{10^{-9.5}} = 10^{-2.5}$

pH 6 $\quad Al^{+3} = \dfrac{10^{-18}}{10^{-9.5}} = 10^{-8.5}$

$$Al(OH)^{+2} + 2H_2O = Al(OH)_3(S) + 2H^+ \qquad K_3 = ?$$

$$K_3 = \frac{(H^+)^2[Al(OH)_3(S)]}{Al\,OH^{+2}} = \frac{[Al(OH)_3(S)](H^+)^3}{Al^{+3}} \times \frac{Al^{+3}}{Al(OH)^{+2}(H^+)}$$

$$K_3 = \frac{K_2}{K_1} = \frac{10^{-9.5}}{10^{-5}} = 10^{-4.5}$$

$$Al\,OH^{+2} = \frac{(H^+)^2}{10^{-4.5}}$$

---

at pH 2 $\quad Al\,OH^{+2} = \dfrac{10^{-4}}{10^{-4.5}} = 10^{-0.5}$

$$\text{pH 4} \qquad Al\,OH^{+2} = \frac{10^{-8}}{10^{-4.5}} = 10^{-3.5}$$

$$\text{pH 6} \qquad Al\,OH^{+2} = \frac{10^{-12}}{10^{-4.5}} = 10^{-7.5}$$

$$Al^{+3} + 2H_2O = Al(OH)_2^{+} + 2H^{+} \qquad K_4 = 10^{-8.56}$$

$$Al(OH)_3(S) = Al^{+3} + 3OH^{-} \qquad K_5 = 10^{-33}$$

$$Al\,OH^{+2} + H_2O = Al\,(OH)_2^{+} + H^{+} \qquad K_6 = ?$$

$$\frac{(Al\,(OH)_2^{+})\,(H^{+})}{AlOH^{+2}} = \frac{(Al\,(OH)_2^{+})\,(H^{+})^2}{Al^{+3}} \Big/ \frac{(AlOH^{+2})(H^{+})}{Al^{+3}}$$

$$K_6 = \frac{K_4}{K_1} = \frac{10^{-8.56}}{10^{-5}} = 10^{-3.56}$$

$$Al(OH)_3 = Al(OH)_2^{+} + OH^{-} \qquad K_7 = ?$$

$$\frac{(Al(OH)_2^{+})(H^{+})}{AlOH^{+2}} \times \frac{(AlOH^{+2})(H^{+})}{Al^{+3}} \times \frac{(Al^{+3})(OH^{-})^3}{Al(OH)_3(S)} =$$

$$\frac{(Al(OH)_2^{+})(H^{+})^2(OH^{-})^3}{[Al(OH)_3(S)](H^{+})^2(OH^{-})^2} = \frac{(Al(OH)_2^{+})(OH^{-})}{[Al(OH)_3(S)](K_w)^2}$$

$$K_7 = \frac{K_5 K_1 K_6}{(K_w)^2} = \frac{10^{-33}10^{-5}10^{-3.56}}{10^{-28}} = 10^{-13.56}$$

$$\frac{Al(OH)_2^{+} = \frac{10^{-13.56}}{OH^{-}}}{}$$

at pH 2 $Al(OH)_2^+ = \frac{10^{-13.56}}{10^{-12}} = 10^{-1.56}$

pH 4 $Al(OH)_2^+ = \frac{10^{-13.56}}{10^{-10}} = 10^{-3.56}$

pH 6 $Al(OH)_2^+ = \frac{10^{-13.56}}{10^{-8}} = 10^{-5.56}$

$Al(OH)_3(S) + H_2O = Al(OH)_4^- + H^+ \qquad K_8 = 10^{-12.7}$

$$Al(OH)_4^- = \frac{10^{-12.7}}{H^+}$$

at pH 2 $Al(OH)_4^- = \frac{10^{-12.7}}{10^{-2}} = 10^{-10.7}$

pH 4 $Al(OH)_4^- = \frac{10^{-12.7}}{10^{-4}} = 10^{-8.7}$

pH 6 $Al(OH)_4^- = \frac{10^{-12.7}}{10^{-6}} = 10^{-6.7}$

$7\ Al^{+3} + 17\ H_2O = Al_7(OH)_{17}^{+4} + 17H^+ \qquad K_9 = 10^{-48.76}$

$$Al_7(OH)_{17}^{+4} = \frac{10^{-48.76}(Al^{+3})^7}{(H^+)^{17}}$$

at pH 4

$Al^{+3} = 10^{-2.5}$

$$Al_7(OH)_{17}^{+4} = \frac{10^{-48.76}10^{-17.5}}{10^{-68}} = 10^{+1.74}$$

at pH 6

$$Al^{+3} = 10^{-8.5}$$

$$Al_7(OH)_{17}^{+4} = \frac{10^{-48.76}10^{-59.5}}{10^{-102}} = 10^{-6.26}$$

$$2Al^{+3} + 2H_2O = Al_2(OH)_2^{+4} \qquad K_{10} = 10^{-7.2}$$

$$\frac{Al_2(OH)_2^{+4}}{} = \frac{10^{-7.2}(Al^{+3})^2}{(H^+)^2}$$

at pH 4

$$Al_2(OH)_2^{+4} = \frac{10^{-7.2}(10^{-2.5})^2}{(10^{-4})^2} = 10^{-4.2}$$

at pH 6

$$Al_2(OH)_2^{+4} = \frac{10^{-7.2}(10^{-8.5})^2}{(10^{-6})^2} = 10^{-12.2}$$

$$13Al^{+3} + 34H_2O = Al_{13}(OH)_{34}^{+5} + 34H^+ \qquad K_{11} = 10^{-97.6}$$

$$\frac{(Al_{13}(OH)_{34}^{+5})(H^+)^{34}}{(Al^{+3})^{13}} = 10^{-97.6}$$

at pH 4

$$\frac{(Al_{13}(OH)_{34}^{+5})}{(Al^{+3})^{13}} = \frac{10^{-97.6}}{(10^{-4})^{34}} = 10^{+42.4}$$

$$Al_{13}(OH)_{34}^{+5} = 10^{+42.4}(10^{-2.5})^{13} = 10^{+9.9}$$

at pH 6

$$\frac{(Al_{13}(OH)_{34}^{+5})}{(Al^{+3})^{+5}} = \frac{10^{-97.6}}{(10^{-6})34} = 10^{+106.4}$$

$$Al_{13}(OH)_{34}^{+5} = 10^{+106.4}(10^{-8.5})13 = 10^{-4.1}$$

CALCULATIONS FOR THE LANTHANUM STABILITY DIAGRAM

$La(OH)_3(S) = La^{+3} + 3\ OH^-$ $\qquad K_1 = -18.9$

$(La^{+3})\ (OH^-)^3 = 10^{-18.9}$ $\qquad \dfrac{La^{+3}}{[La(OH)_3(S)]\ (H^+)^3} = 10^{23.8}$

$$\underline{La^{+3} = \frac{10^{-18.9}}{(OH^-)^3}} \qquad \text{or} \qquad \underline{La^{+3} = 10^{23.8}(H^+)^3}$$

$$\text{at pH 4 } La^{+3} = \frac{10^{-18.9}}{10^{-30}} = 10^{+11.1}$$

$$\text{pH 8 } La^{+3} = \frac{10^{-18.9}}{10^{-18}} = 10^{-.9}$$

$La^{+3} + H_2O = La(OH)^{+2} + H^+$ $\qquad K_2 = -9.0$

$$\frac{(La(OH)^{+2})\ (H^+)}{La^{+3}} \times \frac{(La^{+3})\ (OH^-)^3}{La(OH)_3(S)} = \frac{(La(OH)^{+2})\ (H^+)(OH^-)^3}{LaOH_3(S)} \cdot \frac{k_w}{k_w}$$

$$k_3 = \frac{k_1 k_2}{k_w} = \frac{La(OH)^{+2}(OH^-)^2}{La(OH)_3(S)} = \frac{10^{-19}\ 10^{-9}}{10^{-14}} = 10^{-14}$$

$$\underline{La(OH)^{+2} = \frac{10^{-14}}{(OH^-)^2}}$$

$$\text{at pH 7 } La\ (OH)^{+2} = \frac{10^{-14}}{10^{-14}} = 10^{o}$$

$$\text{pH 10 } La\ (OH)^{+2} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$$

$$La^{+3} + 2H_2O = La(OH)_2^{+} + 2OH^{-} \qquad K_4 = 10^{11}$$

$$\frac{(La(OH)_2^{+})}{(La^{+3})(OH^{-})^2} \times \frac{(La^{+3})(OH^{-})^3}{La(OH)_3(S)} = \frac{(La(OH)_2^{+})(OH^{-})}{La(OH)_3(S)}$$

$$K_5 = K_4K_1 = 10^{11}10^{-18.9} = 10^{-7.9}$$

$$La(OH)_2^{+} = \frac{10^{-7.9}}{(OH^{-})}$$

$$\text{at pH 4 } La(OH)_2^{+} = \frac{10^{-7.9}}{10^{-10}} = 10^{+2.1}$$

$$\text{pH 8 } La(OH)_2^{+} = \frac{10^{-7.9}}{10^{-6}} = 10^{-1.9}$$

$$5\ La^{+3} + 9\ H_2O = La_5(OH)_9^{+6} + 9H^{+} \qquad K_6 = 10^{-71.45}$$

$$\frac{(La_5(OH)_9^{+6})(H^{+})^9}{(La^{+3})^5} = 10^{-71.45}$$

$$La_5(OH)_9^{+6} = \frac{10^{-71.45}(La^{+3})^5}{(H^{+})^9}$$

$$\text{at pH 4 } \quad La^{+3} = 10^{+11.3}$$

$$La_5(OH)_9^{+6} = \frac{10^{-71.45}(10^{11.3})^5}{(10^{-4})^9} = 10^{+21.05}$$

at pH 6 $La^{+3} = 10^{+5.3}$

$$La_5(OH)_9^{+6} = \frac{10^{-71.45}(10^{5.3})^5}{(10^{-6})^9} = 10^{+9.05}$$

$$6\ La^{+3} + 10H_2O = La_6(OH)_{10}^{+8} + 10H^+ \qquad K_7 = 10^{-78.75}$$

$$\frac{(La_6(OH)_{10}^{+8})(H^+)^{10}}{(La^{+3})^6} = 10^{-78.75}$$

$$La_6(OH)_{10}^{+8} = \frac{10^{-78.75}(La^{+3})^6}{(H^+)^{10}}$$

---

at pH 4

$$La_6(OH)_{10}^{+8} = \frac{10^{-78.75}(10^{+11.3})^6}{(10^{-4})^{10}} = 10^{+29.05}$$

at pH 6

$$La_6(OH)_{10}^{+8} = \frac{10^{-78.75}(10^{+5.3})^6}{(10^{-6})^{10}} = 10^{+13.05}$$

CALCULATIONS FOR THE THORIUM STABILITY DIAGRAM

$$Th(OH)_4(S) = Th^{+4} + 4OH^- \qquad K_1 = 10^{-44.9}$$

$$Th^{+4} = \frac{10^{-44.9}}{(OH^-)^4}$$

at pH 4 $\quad Th^{+4} = \frac{10^{-44.9}}{(10^{-10})^4} = 10^{-4.9}$

pH 6 $\quad Th^{+4} = \frac{10^{-44.9}}{(10^{-8})^4} = 10^{-12.9}$

$$Th^{+4} + H_2O = Th(OH)^{+3} + H^+ \qquad K_2 = 10^{-4.3}$$

$$\frac{(Th(OH)^{+3})(H^+)}{(Th^{+4})} \times \frac{(Th^{+4})(OH^-)^4}{Th(OH)_4(S)} = \frac{(Th(OH)^{+3})(H^+)(OH^-)^4}{Th(OH)_4(S)}$$

$$Ka = K_1K_2 = 10^{-44.9}\ 10^{-4.3} = 10^{-49.2}$$

$$Th(OH)^{+3} = \frac{10^{-49.2}}{(H^+)(OH^-)^4}$$

at pH 4 $\quad Th(OH)^{+3} = \frac{10^{-49.2}}{10^{-4}(10^{-40})} = 10^{-5.2}$

pH .6 $\quad Th(OH)^{+3} = \frac{10^{-49.2}}{10^{-6}\ 10^{-32}} = 10^{-11.2}$

$$Th(OH)^{+3} + H_2O = Th(OH)_2^{+2} + H^+ \qquad K_3 = 10^{-4.02}$$

$$\frac{(Th(OH)_2^{+2})(H^+)}{Th(OH)^{+3}} \times \frac{(Th(OH)^{+3})(H^+)}{Th^{+4}} \times \frac{Th^{+4}(OH^-)^4}{Th(OH)_4(S)} = \frac{Th(OH)_2^{+2}(H^+)^2(OH^-)^4}{Th(OH)_4(S)}$$

$$= K_b = K_1K_2K_3 = 10^{-53.22}$$

$$Th(OH)_2^{+2} = \frac{10^{-53.22}}{K_w^{\,2}(OH^-)^2}$$

at pH 4 $\quad Th(OH)_2^{+2} = \dfrac{10^{-53.22}}{10^{-28}10^{-20}} = 10^{-5.22}$

pH 6 $\quad Th(OH)_2^{+2} = \dfrac{10^{-53.22}}{10^{-28}10^{-16}} = 10^{-9.22}$

$$Th(OH)_4(S) + H^+ = Th(OH)_3^+ \qquad K_4 = 1.51$$

$$Th(OH)_3^+ = 10^{1.51}(H^+)$$

at pH 4 $\quad Th(OH)_3^+ = 10^{1.51}10^{-4} = 10^{-2.49}$

pH 6 $\quad Th(OH)_3^+ = 10^{1.51}10^{-6} = 10^{-4.49}$

$$Th(OH)_4(S) + OH^- = Th(OH)_5^- \qquad K_5 = 10^{-5.8}$$

$$Th(OH)_5^- = 10^{-5.8}(OH^-)$$

at pH 10 $\quad Th(OH)_5^- = 10^{-5.8}10^{-4} = 10^{-9.8}$

pH 8 $\quad Th(OH)_5^- = 10^{-5.8}10^{-6} = 10^{-11.8}$

$$Th(OH)_4(S) + 2OH^- = Th(OH)_6^{-2} \qquad K_6 = 10^{-5.8}$$

$$Th(OH)_6^{-2} = 10^{-5.8}(OH^-)^2$$

at pH 6 $\quad Th(OH)_6^{-2} = 10^{-21.8}$

pH 10 $\quad Th(OH)_6^{-2} = 10^{-13.8}$

$$\frac{(Th_2^{+4}(OH)_2^{+6})(H^+)^2}{(Th^{+4})^2} = 10^{-5.02} = K_7$$

$$\frac{(Th_2(OH)_2^{+6})(H^+)^2}{(Th^{+4})^2} \times \frac{(Th^{+4})^2(OH^-)^8}{[Th(OH)_4(S)]^2} = \frac{Th_2(OH)_2^{+6}(H_2^+)^2(OH^-)^8}{[Th(OH)_4(S)]^2}$$

$$K_c = K_1^2 K_7 = 10^{-5.02}(10^{-44.9})^2 = 10^{-94.82}$$

$$Th_2(OH)_2^{+6} = \frac{10^{-94.82}}{(H^+)^2(OH^-)^8}$$

at pH 4 $\quad Th_2(OH)_2^{+6} = 10^{-6.82}$

pH 6 $\quad Th_2(OH)_2^{+6} = 10^{-18.82}$

$$\frac{Th_2(OH)^{+7}(H^+)}{(Th^{+4})^2(H_2O)} = K_8 = 10^{-2.8}$$

$$\frac{(Th_2(OH)^{+7})(H^+)}{(Th^{+4})^2} \times \frac{(Th^{+4})^2[(OH^-)^4]^2}{[Th(OH)_4(S)]^2} = \frac{(Th_2(OH)^{+7})(OH^-)^8(H^+)}{[Th(OH^-)_4(S)]^2}$$

$$K_d = K_1^2 K_8 = (10^{-44.9})^2(10^{-2.8}) = 10^{-92.6}$$

$$Th_2(OH)^{+7} = \frac{K_d}{(OH^-)^8(H^+)}$$

at pH 4 $\quad Th_2(OH)^{+7} = 10^{-8.6}$

pH 6 $\quad Th_2(OH)^{+7} = 10^{-22.6}$

$$5Th^{+4} + 12H_2O = Th_5(OH)_{12}^{+8} + 12H^+ \qquad K_9 = 10^{-29.5}$$

$$\frac{Th_5(OH)_{12}^{+8}(H^+)^{12}}{(Th^{+4})^5} \times \frac{(Th^{+4})^5(OH^-)^{20}}{[Th(OH)_4(S)]^5} = \frac{(Th_5(OH)_{12}^{+8})(H^+)^{12}(OH)^{20}}{[Th(OH)_4(S)]^5}$$

$$K_e = K_g k_1^5 = 10^{-29.5}\,(10^{-44.9})^5 = 10^{-254}$$

$$Th_5(OH)_{12}^{+8} = \frac{K_e}{(H^+)^{12}(OH^-)^{20}} = \frac{K_e}{K_w^{12}\,(OH^-)^8}$$

at pH 4 $\quad Th_5(OH)_{12}^{+8} = 10^{-6}$

pH 6 $\quad Th_5(OH)_{12}^{+8} = 10^{-22}$

APPENDIX II

```
      JAR TEST PROGRAM
RUNX(S)
SETCORE.
LGO.
-
      PROGRAM JTEST(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)                    1
C
C
C
      DIMENSION PH(20),PERCENT(20),TOC(20),EDTATO(15),EDTACA(15),             2
     1AA(20,20),BB(20,20),XX(20,20),P(20),                                    3
     2PLOT(200),PHPLT(201),PTPLT(201),TOCPLT(201)                            4
      REAL MG1,MG2                                                            5
C
C
C
      II = 6
      DO 1000 JJ=1,II                                                         7
      READ(5,10) DATE,SAMDATE,COAG,CONC,SAMVOL,EDTADF,FACTOR,N,START          8
   10 FORMAT(3A10,4F10.0,I2,F8.0)                                             9
      READ(5,20) (PH(I),I=1,N)                                               10
      READ(5,20) (PERCENT(I),I=1,N)                                          11
      READ(5,20) (TOC(I),I=1,N)                                              12
      READ(5,20) (EDTATO(I),I=1,N)                                           13
      READ(5,20) (EDTACA(I),I=1,N)                                           14
   20 FORMAT(12F6.3)                                                         15
C
      PH(N+1)=0.5$PH(N+2)=1.0$PH(N+3)=11.0$PH(N+4)=12.0                      16
      N1=N+1                                                                 17
      N2=N+4                                                                 18
      DO 25 I=N1,N2                                                          19
      PERCENT(I)=50.0                                                        20
      TOC(I)=36.0                                                            21
   25 CONTINUE                                                               22
C
      WRITE(6,30) DATE,SAMDATE,COAG,CONC,SAMVOL,EDTADF,FACTOR                23
   30 FORMAT(1H1,20X,18HDATE OF EXPERIMENT,2X,16HDATE OF SAMPLING,4X,         24
     114HCOAGULANT USED,6X,13HCONCENTRATION,/                                25
     21H0,20(,3(A10,10X),F5.1,2X,16H(MG/L OF SAMPLE),//                      26
     31H0,20(,14HTITRATION VOL.,6X,16HEDTA DIL. FACTOR,4X,                   27
     411HEDTA FACTOR,/                                                       28
     51H0,20(,F4.1,2X,2HML,12X,F4.1,15X,F8.5,//)                             29
C
      SUM1=0.                                                                30
      SUM2=0.                                                                31
      DO 100 I=1,N                                                           32
      SUM1=SUM1+EDTATO(I)                                                    33
      SUM2=SUM2+EDTACA(I)                                                    34
  100 CONTINUE                                                               35
C
      TOHARD=(SUM1/N)*(1./EDTADF)*(1000./SAMVOL)*1.001*FACTOR                36
      CA1=(SUM2/N)*(1./EDTADF)*(1000./SAMVOL)*1.001*FACTOR                   37
      CA2=CA1*(0.401/1.001)                                                  38
      MG1=TOHARD-CA1                                                         39
      MG2=MG1*(0.243/1.001)                                                  40
C
```

```
      WRITE(6,90) TOHARD,CA1,CA2,MG1,MG2                                41
   90 FORMAT(1HO,20X,18HTOTAL HARDNESS   = ,F8.3,3X,13HMG/L AS CACO3,/  42
     11HO,20X,18HCALCIUM CONC.    = ,F8.3,3X,13HMG/L AS CACO3,/          43
     21HO,20X,18HCALCIUM CONC.    = ,F8.3,3X,15HMG/L AS CALCIUM,/        44
     31HO,20X,18HMAGNESIUM CONC. = ,F8.3,3X,13HMG/L AS CACO3,/          45
     41HO,20X,18HMAGNESIUM CONC. = ,F8.3,3X,17HMG/L AS MAGNESIUM//)     46
      WRITE(6,40)                                                       47
   40 FORMAT(1HO,20X,17HORIGINAL DATA ARE,/                             49
     11HO,22X,2HPH,6X,13HTRANSMITTANCE,6X,15HTOTAL O. CARBON,5X,        49
     214HT.P. EDTA (ML),6X,17HCALCIUM EDTA (ML))                        50
      DO 50 I=1,N                                                       51
      WRITE(6,60) PH(I),PERCENT(I),TOC(I),EDTATO(I),EDTACA(I)           52
   60 FORMAT(1HO,20X,F5.2,5X,4(5X,F5.2,10X))                            53
   50 CONTINUE                                                          54
C
      DO 500 NN=1,2                                                     55
      M=6                                                               56
      MX2=M*2                                                           57
      MM=M+1                                                            58
C
C     GENERATE POWER (P) ARRAY FOR LEAST SQUARE EQUATIONS
C
      DO 130 I=1,MX2                                                    59
      P(I)=0.                                                           60
      DO 130 J=1,N2                                                     61
      P(I)=P(I)+PH(J)**I                                                62
  130 CONTINUE                                                          63
C
C     NOW USE THE (P) ARRAY TO GENERATE (AA) ARRAY FOR MATRIX (SIMULTANEOUS
C     EQUATIONS) CALCULATIONS
C
      AA(1,1)=N2                                                        64
      DO 140 I=1,MM                                                     65
      DO 140 J=1,MM                                                     66
      L=I+J-2                                                           67
      IF(L.EQ.0) GO TO 140                                              68
      AA(I,J)=P(L)                                                      69
  140 CONTINUE                                                          70
C
C     NOW GENERATE THE (BB) COLUMN VECTOR ARRAY
C
      DO 150 I=1,MM                                                     71
      BB(I)=0.                                                          72
      DO 150 J=1,N2                                                     73
      IF(MOD(NN,2).NE.0) GO TO 160                                      74
      BB(I)=BB(I)+TOC(J)*PH(J)**(I-1)                                   75
      GO TO 150                                                         76
  160 BB(I)=BB(I)+PERCENT(J)*PH(J)**(I-1)                               77
  150 CONTINUE                                                          78
C
C     NOW SOLVE THE SYSTEM (AA)*(C)=(BB) FOR THE COEFFICIENT VECTOR (C)
C
C
      CALL GEBS(AA,BB,MM,1,K,XX)                                        79
C
C
```

```
C      SOLUTION (C) VECTOR IS RETURNED IN (XX) LOCATION FROM SUBROUTINE GEBS
C
       IF(ABS(AA(K,K)).LE.1C.**(-10)) GO TO 500                          80
       IF(ABS(AA(NN,MM)).LE.10.**(-10)) GO TO 500                        81
       IF(MOD(NN,2).NE.0) GO TO 170                                      82
       WRITE(6,165) M,(I,XX(I),I=1,MM)                                   83
  165  FORMAT(1HC,20X,25HREQUIRED COEFFICIENTS FOR,I3,2X,2HTH,1X,6HORDER  84
      1/,1HC,20X,43HPOLYNOMIAL FOR PH VS. TOTAL ORGANIC CARBON ,//       85
      21HC,21X,1HI,19X,4HC(I),/(1HC,I22,10X,E20.8))                      86
       GO TO 180                                                         87
  170  WRITE(6,175) M,(I,XX(I),I=1,MM)                                   88
  175  FORMAT(1HI,20X,25HREQUIRED COEFFICIENTS FOR,I3,2X,2HTH,1X,6HORDER  89
      1/,1HC,20X,44HPOLYNOMIAL FOR PH VS. PERCENT TRANSMITTANCE ,//      90
      21HC,21X,1HI,19X,4HC(I),/(1HC,I22,10X,E20.8)//)                    91
C
  180  PHMIN=START                                                       92
       PHMAX=START+10.0                                                  93
       PTMIN=0.                                                          94
       PTMAX=100.                                                        95
       H=(PHMAX-PHMIN)/200.                                              96
       DO 200 J=1,201                                                    97
       PHPLT(J)=PHMIN+H*FLOAT(J-1)                                       98
       IF(MOD(NN,2).NE.0) GO TO 220                                      99
       TOCPLT(J)=XX(1)                                                  100
       DO 210 I=2,MM                                                    101
       TOCPLT(J)=TOCPLT(J)+XX(I)*PHPLT(J)**(I-1)                        102
  210  CONTINUE                                                         103
C
       GO TO 200                                                        104
  220  PTPLT(J)=XX(1)                                                   105
       DO 230 I=2,MM                                                    106
       PTPLT(J)=PTPLT(J)+XX(I)*PHPLT(J)**(I-1)                          107
  230  CONTINUE                                                         108
  200  CONTINUE                                                         109
C
       IF(MOD(NN,2).NE.0) GO TO 500                                     110
       WRITE(6,250)                                                     111
  250  FORMAT(1H1,20X,75HPH - PERCENT TRANSMITTANCE, PH - TOTAL ORGANIC C112
      1ARBON REMAINED RELATIONSHIP,//                                   113
      21HC,26X,2HPH,19X,19HPERCENT T.,15X,16HTOTAL O.C.(MG/L))          114
       DO 260 J=1,201,10                                                115
       WRITE(6,270) PHPLT(J),PTPLT(J),TOCPLT(J)                         116
  270  FORMAT(1HC,24X,F6.3,2(17X,F10.5))                                117
  260  CONTINUE                                                         118
C
C
       CALL PLOT 2 (PLOT,PHMAX,PHMIN,PTMAX,PTMIN)                       119
       CALL PLOT 3 (1H*,PHPLT,PTPLT,200)                                120
       CALL PLOT 3 (1HP,PH,PERCENT,N)                                   121
       CALL PLOT 3 (1H.,PHPLT,TOCPLT,200)                               122
       CALL PLOT 3 (1HC,PH,TOC,N)                                       123
C
C
       WRITE(6,280) M,N,DATE,SAMDATE,COAG,CONC                          124
  280  FORMAT(1H1,10X,62HCURVE FITTING RESULTS FOR PH - P.T., PH -T.O.C. 125
      1RELATIONSHIP,,3X,I4,1X,19HTH ORDER POLYNOMIAL,                   126
```

```
     23X,11HDATA POINTS,I5,/1H0,20X,18HDATE OF EXPERIMENT,                  127
     32X,16HDATE OF SAMPLING,4X,14HCOAGULANT USED,6X,13HCONCENTRATION,/     128
     41H ,20(,3(A10,10X),F5.1,2X,16H(MG/L OF SAMPLE))                       129
C
C
      CALL PLOT 4(43,43H           TRANSMITTANCE           TOC...MG/L)       130
C
C
      WRITE(6,400)                                                          131
  400 FORMAT(1H ,62X,2HPH,/                                                 132
     11H ,10X,21HPPP = GIVEN P.T. DATA,5X,23HCCC = GIVEN T.O.C. DATA,       133
     25X,24H*** = CURVE FIT FOR P.T.,5X,26H... = CURVE FIT FOR T.O.C.)      134
  500 CONTINUE                                                              135
 1000 CONTINUE                                                              136
      STOP                                                                  137
      END                                                                   138
      SUBROUTINE GEBS(A,B,N,NB,K,X)                                           1
C
C
C
      DIMENSION A(20,20),B(20,10),X(20,10)                                    2
C
C
C     THIS IS SUBROUTINE GEBS (GAUSS ELIMINATION BACK SUBSTITUTION)
C     FOR SOLVING SIMULTANEOUS EQUATIONS(MATRICES).
C
C
C     DESCRIPTION OF VARIABLES
C
C
C     A..........NAME OF COEFFICIENT MATRIX ARRAY
C     B..........NAME OF CONSTANT MATRIX ARRAY
C     X..........NAME OF SOLUTION MATRIX ARRAY
C
C
      N1=N-1                                                                  3
      M=1                                                                     4
   50 DO 15 K=1,N1                                                            5
C
C
      CALL INTER (K,N,NB,A,B,M)                                               6
C
C
   10 II=K+1                                                                  7
      M=M+1                                                                   8
      DO 15 I=II,N                                                            9
      IF(ABS(A(K,K)).LE.10.**(-10)) GO TO 26                                 10
      EM= A(I,K)/A(K,K)                                                      11
      A(I,K)=0.                                                              12
      L=K+1                                                                  13
      DO 20 J=L,N                                                            14
      A(I,J)=A(I,J)-EM*A(K,J)                                                15
   20 CONTINUE                                                               16
C
      DO 15 L=1,NB                                                           17
      B(I,1)=B(I,L)-EM*B(K,L)                                                18
```

```
   15 CONTINUE                                                          19
C
C     THE BACK SUBSTITUTION STARTS HERE
C
      DO 25 L=1,NB                                                      20
      IF(ABS(A(N,N)).LE.10.**(-10)) GO TO 26                            21
      X(N,L)= B(N,L)/A(N,N)                                             22
      DO 25 K=1,N1                                                      23
      I= N-K                                                            24
      S=0.                                                              25
      II=I+1                                                            26
      DO 30 J=II,N                                                      27
      S=S+A(I,J)*X(J,L)                                                 28
   30 CONTINUE                                                          29
C
      X(I,1)=(B(I,L)-S)/A(I,I)                                          30
   25 CONTINUE                                                          31
C
      GO TO 7                                                           32
   26 WRITE(6,27)                                                       33
   27 FORMAT(1HO,20X,43HSINGULAR POINT EXISTS, NO FEASIBLE SOLUTION/)   34
    7 RETURN                                                            35
      END                                                               36
      SUBROUTINE INTER (K,N,NB,A,B,M)                                   1
C
C
C
C     THIS SUBROUTINE INTERCHANGES ROWS FOR GAUSS ELIMINATION METHOD,
C     GAUSS-JORDAN METHOD, ETC.
C
C     INPUT IS A AND B MATRICES
C     OUTPUT IS REARRANGED A AND B MATRICIES.
C
C
C     DESCRIPTION OF VARIABLES
C
C
C     NB.....NUMBER OF B VECTORS
C     K......INDEX OF COLUMN BEING ELIMINATED
C     J......COLUMN INDEX
C     I......ROW INDEX
C     M......DUMMY VARIABLE TO IDENTIFY THE NUMBER OF INTERCHANGE
C            NECESSARY FOR ONE SET OF MATRICES
C
C
C
      DIMENSION A(20,20),B(20,10)                                       2
C
C
      L=K                                                               3
      II=K+1                                                            4
      DO 10 I=II,N                                                      5
      IF(ABS(A(I,K)).GT.ABS(A(L,K))) L=I                                6
   10 CONTINUE                                                          7
      IF(L.EQ.K) GO TO 101                                              8
      DO 20 J=K,N                                                       9
```

```
      TEMP= A(K,J)                                                      10
      A(K,J)=A(L,J)                                                     11
      A(L,J)=TEMP                                                       12
   20 CONTINUE                                                          13
C
      DO 30 J =1,NB                                                     14
      TEMP =B(K,J )                                                     15
      B(K,J )=B(L,J )                                                   16
      B(L,J)=TEMP                                                       17
   30 CONTINUE                                                          18
  101 RETURN                                                            19
      END                                                               20
-
```

```
      COLLOID TITRATION PROGRAM
RUNX(S)
SETCORE.
LGO.
-
      PROGRAM COLLOID(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C
C
      DIMENSION SAMPH(50),SAMPVSK(50),BLKPH(50),BLKPVSK(50),                1
     1PLOT(900),SAMPLT(201),BLKPLT(201),CHARGE(201),PHPLT(201),             2
     2COMMENT(10),A(20,20),B(20),P(40)                                      3
C
C
C
      II = 2                                                                4
      DO 50 NSET=1,II                                                       5
      M = 6                                                                 6
      MX2=M*2                                                               7
      N=M+1                                                                 8
      VOL=20.                                                               9
      DO 50 JJ=1,2                                                          10
      IF(MOD(JJ,2).NE.0) GO TO 3                                            11
      WRITE(6,1)                                                            12
    1 FORMAT(1H1,20X,35HGIVEN DATA FOR BLANK TITRATION ARE ,//)             13
      GO TO 4                                                               14
    3 READ(5,1000) (COMMENT(I),I=1,10),START                                15
 1000 FORMAT(10A7,F10.0)                                                    16
      WRITE(6,1010) (COMMENT(I),I=1,10),START                               17
 1010 FORMAT(1H1,20X,10A7/1H0,20X,25HLOWER LIMIT FOR PVSK PLOT,2X,F3.1,     18
     12X3HML.)                                                              19
      WRITE(6,2)                                                            20
    2 FORMAT(//1H0,20X,35HGIVEN DATA FOR SAMPLE TITRATION ARE,//)           21
    4 WRITE(6,5)                                                            22
    5 FORMAT(1H0,30X,2HPH,38X,13HPVSK REQUIRED,/                            23
     11H0,14X,5HPH(1),10X,5HPH(2),10X,5HPH(3),                              24
     29X,7HPVSK(1),8X,7HPVSK(2),8X,7HPVSK(3))                               25
      DO 11 I=1,50,3                                                        26
      KK=I+2                                                                27
      IF(MOD(JJ,2).NE.0) GO TO 9                                            28
      READ(5,7) (BLKPH(I),I=I,KK), (BLKPVSK(I),I=I,KK)                      29
    7 FORMAT(6(F10.4))                                                      30
      IF(BLKPH(I).EQ.0.) GO TO 12                                           31
      WRITE(6,20) (BLKPH(I),I=I,KK), (BLKPVSK(I),I=I,KK)                    32
   20 FORMAT(1H0,10X,6(F10.5,5X))                                           33
      GO TO 11                                                              34
    9 READ(5,10) (SAMPH(I),I=I,KK), (SAMPVSK(I),I=I,KK)                     35
   10 FORMAT(6(F10.4))                                                      36
      IF(SAMPH(I).EQ.0.) GO TO 12                                           37
      WRITE(6,25) (SAMPH(I),I=I,KK), (SAMPVSK(I),I=I,KK)                    38
   25 FORMAT(1H0,10X,6(F10.5,5X))                                           39
   11 CONTINUE                                                              40
C
C     GENERATE POWER (P) ARRAY FOR LEAST SQUARE EQUATIONS
C
   12 NN=I-1                                                                41
      DO 13 I=1,MX2                                                         42
```

```
      P(I)=0.                                                                  43
      DO 13 J=1,NN                                                             44
      IF(MOD(JJ,2).NE.0) GO TO 18                                              45
      P(I)=P(I)+BLKPH(J)**I                                                    46
      GO TO 13                                                                 47
   18 P(I)=P(I)+SAMPH(J)**I                                                    48
   13 CONTINUE                                                                 49
C
C     NOW USE THE (P) ARRAY TO GENERATE THE (A) ARRAY FOR MATRIX (SIMULTANFOUS
C     EQUATIONS) CALCULATION
C
      A(1,1)=NN                                                                50
      DO 30 I=1,N                                                              51
      DO 30 J=1,N                                                              52
      K=I+J-2                                                                  53
      IF(K.EQ.0) GO TO 30                                                      54
      A(I,J)=P(K)                                                              55
   30 CONTINUE                                                                 56
C
C     NOW GENERATE THE (B) COLUMN VECTOR ARRAY
C
      DO 21 I=1,N                                                              57
      B(I)=0.                                                                  58
      DO 21 J=1,NN                                                             59
      IF(MOD(JJ,2).NE.0) GO TO 15                                              60
      B(I)=B(I)+BLKPVSK(J)*BLKPH(J)**(I-1)                                     61
      GO TO 21                                                                 62
   15 B(I)=B(I)+SAMPVSK(J)*SAMPH(J)**(I-1)                                     63
   21 CONTINUE                                                                 64
C
C     NOW SOLVE THE SYSTEM (A)*(C)=(B) FOR THE COFFFICIENT VECTOR (C)
C
C
      CALL INVR(A,N,B,1,DET,20,20)                                             65
C
C
C     SOLUTION((C) VECTOR) IS RETURNED IN (B) LOCATION FROM SUBROUTINE INVR
C
      WRITE(6,91) DET                                                          66
   91 FORMAT(1H0,/ ,20X,25HTHE SYSTEM DETERMINANT IS,5X,E15.8,//)              67
      WRITE(6,90)M,(I,B(I),I=1,N)                                              68
   90 FORMAT(1H0,20X,50HREQUIRED COFFFICIENTS FOR THE POLYNOMIAL OF DEGR       69
     1EE,I3,//1H0,21X,1HI,19X,4HC(I),/(1H0,I22,10X,E20.8))                     70
      PHMIN=2.                                                                 71
      PHMAX=12.                                                                72
      PVSKMIN=START                                                            73
      PVSKMAX=START+3.0                                                        74
      CRGMIN=-0.3                                                              75
      CRGMAX=0.2                                                               76
      H=(PHMAX-PHMIN)/200.                                                     77
      DO 112 J=1,201                                                           78
      PHPLT(J)=PHMIN+H*FLOAT(J-1)                                              79
      IF(MOD(JJ,2).NE.0) GO TO 101                                             80
      BLKPLT(J)=B(1)                                                           81
      DO 110 I=2,N                                                             82
      BLKPLT(J)=BLKPLT(J)+B(I)*PHPLT(J)**(I-1)                                 83
  110 CONTINUE                                                                 84
```

```
C
      GO TO 112
  101 SAMPLT(J)=B(1)                                                    85
      DO 105 I=2,N                                                      86
      SAMPLT(J)=SAMPLT(J)+B(I)*PHPLT(J)**(I-1)                          87
  105 CONTINUE                                                          88
  112 CONTINUE                                                          89
C
      IF(MOD(JJ,2).NE.0) GO TO 50                                       90
      WRITE(6,117)                                                      91
  117 FORMAT(1H1,20X,34HPH - PVSK REQUIREMENT RELATIONSHIP,//,          92
     1 1H0,16X,2HPH,15X,16HSAMPLE PVSK-(ML),10X,15HBLANK PVSK-(ML),     93
     2 9X,14HCHARGE-(MEQ/L))                                            94
      DO 116 J=1,201                                                    95
      CHARGE(J)=(SAMPLT(J)-BLKPLT(J))*(1./200.)*(1000./VOL)             96
  116 CONTINUE                                                          97
C
      DO 119 J=1,201,10                                                 98
      WRITE(6,118)PHPLT(J),SAMPLT(J),BLKPLT(J),CHARGE(J)                99
  118 FORMAT(1H0,14X,F6.3,3(17X,F8.5))                                 100
  119 CONTINUE                                                         101
C
C
C
      CALL PLOT 2 (PLOT,PHMAX,PHMIN,PVSKMAX,PVSKMIN)                   102
      CALL PLOT 3 (1H*,PHPLT,SAMPLT,200)                               103
      CALL PLOT 3 (1HS,SAMPH,SAMPVSK,NN)                               104
      CALL PLOT 3 (1H.,PHPLT,BLKPLT,200)                               105
      CALL PLOT 3 (1HB,BLKPH,BLKPVSK,NN)                               106
C
C
C
      WRITE(6,120) M,NN,(COMMENT(I),I=1,10)                            107
  120 FORMAT(1H1,  10X,69HCURVE FITTING RESULTS FOR PVSK - PH RELATIONSH 108
     1IP FOR SAMPLE AND BLANK,3X,19HORDER OF POLYNOMIAL,I4,3X,11HDATA PO 109
     2INTS,I5,/1H ,20X,10A7)                                           110
C
C
      CALL PLOT 4 (35,35H          0.005N PVSK REQUIRED...ML)          111
C
C
      WRITE(6,121)                                                     112
  121 FORMAT(1H0,62X,2HPH,/                                            113
     1 1H ,10X,25HSSSSS = GIVEN SAMPLE DATA,3X,                        114
     2         25HBBBBB = GIVEN BLANK DATA ,3X,                        115
     3         25H***** = SAMPLE CURVE FIT ,3X,                        116
     4         25H..... = BLANK CURVE FIT  )                           117
C
C
      CALL PLOT 2 (PLOT,PHMAX,PHMIN,CRGMAX,CRGMIN)                     118
      CALL PLOT 3 (1H.,PHPLT,CHARGE,200)                               119
C
C
      WRITE(6,130) (COMMENT(I),I=1,10)                                 120
  130 FORMAT(1H1,/,40X,50HCURVE FITTING RESULTS FOR CHARGE - PH RELATION 121
     1SHIP,/1H ,20X,10A7)                                              122
C
C
```

```
      CALL PLOT 4 (34,34H                          CHARGE...MEQ/L)                  123
C
C
      WRITE(6,131)                                                                  124
  131 FORMAT(1H0,62X,2HPH,/1H0,20X,23H..... = COMPUTED CHARGE)                      125
   50 CONTINUE                                                                      126
      STOP                                                                          127
      END                                                                           128
      SUBROUTINE INVR(A,N,B,M,DETERM,ISIZE,JSIZE)
C
C
C
      DIMENSION IPIVOT(100),A(ISIZE,JSIZE),B(ISIZE,M),INDEX(100,2),
C
C
C     DESCRIPTION OF VARIABLES
C
C
C     A...........NAME OF COEFFICIENT MATRIX ARRAY
C     B...........NAME OF CONSTANT MATRIX ARRAY
C     X...........NAME OF SOLUTION MATRIX ARRAY
C
C
     1IPIVOT(100)
C
      EQUIVALENCE (IROW,JROW),(ICOLUM,JCOLUM),(AMAX,T,SWAP)
C                                                                          INVR  10
C
C
   10 DETERM=1.0                                                           INVR  11
   15 DO 20 J=1,N                                                          INVR  12
   20 IPIVOT(J)=0                                                          INVR  13
   30 DO 550 I=1,N                                                         INVR  14
C                                                                          INVR  15
C     SEARCH FOR PIVOT ELEMENT                                             INVR  16
C                                                                          INVR  17
   40 AMAX=0.0                                                             INVR  18
   45 DO 105 J=1,N                                                         INVR  19
   50 IF (IPIVOT(J)-1) 60, 105, 60                                         INVR  20
   60 DO 100 K=1,N                                                         INVR  21
   70 IF (IPIVOT(K)-1) 80, 100, 740                                        INVR  22
   80 IF(ABS(AMAX)-ABS(A(J,K)))85,100,100
   85 IROW=J                                                               INVR  24
   90 ICOLUM=K                                                             INVR  25
   95 AMAX=A(J,K)                                                          INVR  26
  100 CONTINUE                                                             INVR  27
  105 CONTINUE                                                             INVR  28
  110 IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1                                      INVR  29
C                                                                          INVR  30
C     INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL                    INVR  31
C                                                                          INVR  32
  130 IF (IROW-ICOLUM) 140, 260, 140                                       INVR  33
  140 DETERM=-DETERM                                                       INVR  34
  150 DO 200 L=1,N                                                         INVR  35
  160 SWAP=A(IROW,L)                                                       INVR  36
  170 A(IROW,L)=A(ICOLUM,L)                                                INVR  37
  200 A(ICOLUM,L)=SWAP                                                     INVR  38
```

```
  205 IF(M) 260, 260, 210                                                INVR  39
  210 DO 250 L=1, M                                                      INVR  40
  220 SWAP=B(IROW,L)                                                     INVR  41
  230 B(IROW,L)=B(ICOLUM,L)                                              INVR  42
  250 B(ICOLUM,L)=SWAP                                                   INVR  43
  260 INDEX(I,1)=IROW                                                    INVR  44
  270 INDEX(I,2)=ICOLUM                                                  INVR  45
  310 PIVOT(I)=A(ICOLUM,ICOLUM)                                          INVR  46
  320 DETERM=DETERM*PIVOT(I)                                             INVR  47
      IF(ABS(DETERM).LE.10.**(-10)) GO TO 740
C                                                                        INVR  48
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT                                  INVR  49
C                                                                        INVR  50
  330 A(ICOLUM,ICOLUM)=1.0                                               INVR  51
  340 DO 350 L=1,N                                                       INVR  52
  350 A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)                                   INVR  53
  355 IF(M) 380, 380, 360                                                INVR  54
  360 DO 370 L=1,M                                                       INVR  55
  370 B(ICOLUM,L)=B(ICOLUM,L)/PIVOT(I)                                   INVR  56
C                                                                        INVR, 57
C     REDUCE NON-PIVOT ROWS                                              INVR  58
C                                                                        INVR  59
  380 DO 550 L1=1,N                                                      INVR  60
  390 IF(L1-ICOLUM) 400, 550, 400                                        INVR  61
  400 T=A(L1,ICOLUM)                                                     INVR  62
  420 A(L1,ICOLUM)=0.0                                                   INVR  63
  430 DO 450 L=1,N                                                       INVR  64
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T                                      INVR  65
  455 IF(M) 550, 550, 460                                                INVR  66
  460 DO 500 L=1,M                                                       INVR  67
  500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T                                      INVR  68
  550 CONTINUE                                                           INVR  69
C                                                                        INVR  70
C     INTERCHANGE COLUMNS                                                INVR  71
C                                                                        INVR  72
  600 DO 710 I=1,N                                                       INVR  73
  610 L=N+1-I                                                            INVR  74
  620 IF (INDEX(L,1)-INDEX(L,2)) 630, 710, 630                           INVR  75
  630 JROW=INDEX(L,1)                                                    INVR  76
  640 JCOLUM=INDEX(L,2)                                                  INVR  77
  650 DO 705 K=1,N                                                       INVR  78
  660 SWAP=A(K,JROW)                                                     INVR  79
  670 A(K,JROW)=A(K,JCOLUM)                                              INVR  80
  700 A(K,JCOLUM)=SWAP                                                   INVR  81
  705 CONTINUE                                                           INVR  82
  710 CONTINUE                                                           INVR  83
  740 RETURN                                                             INVR  84
      END                                                                INVR  85
```

ALUMINUM 20

CALCIUM 0

MAGNESIUM 0

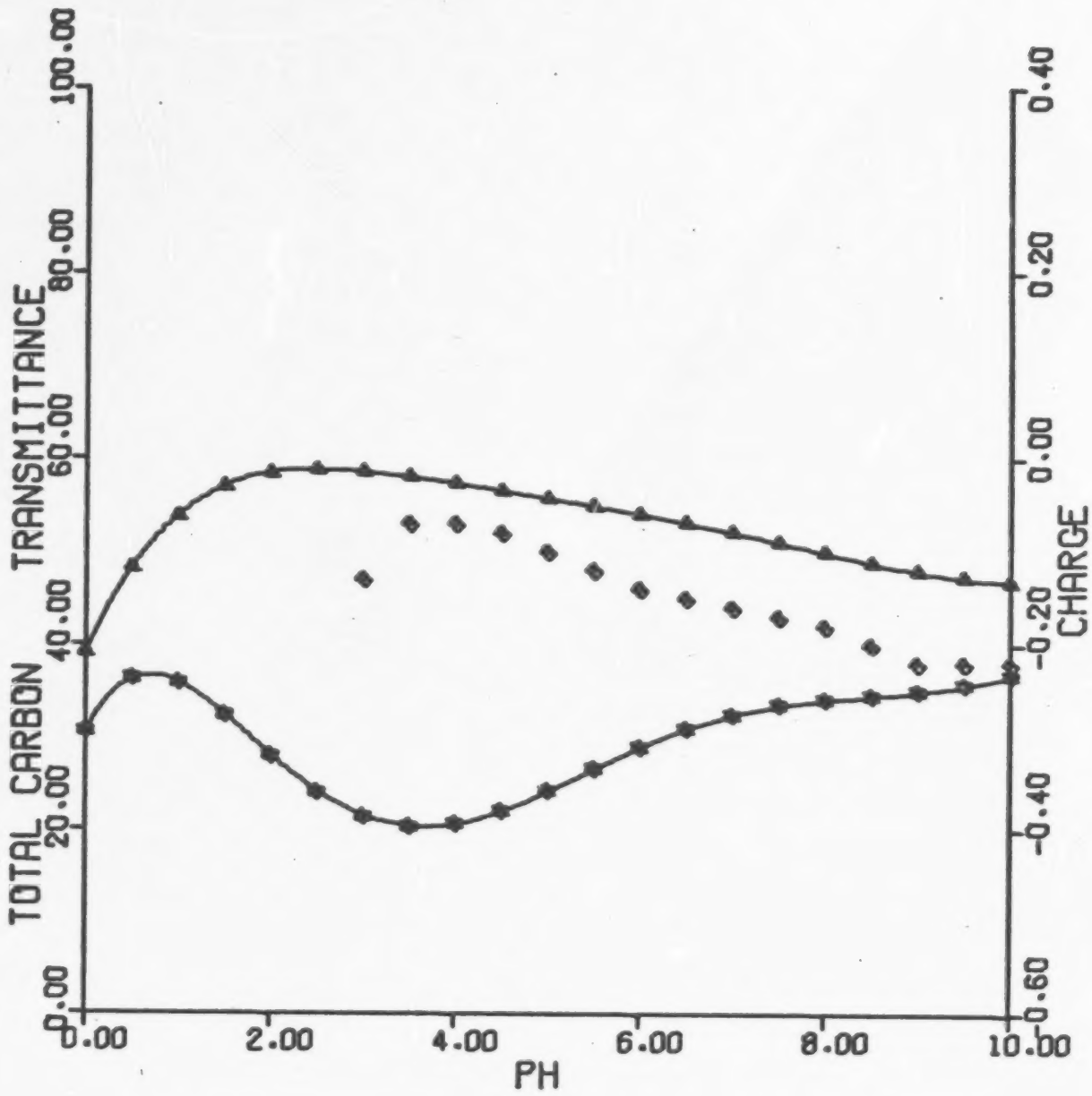


Figure 1

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 40

CALCIUM 0

MAGNESIUM 0

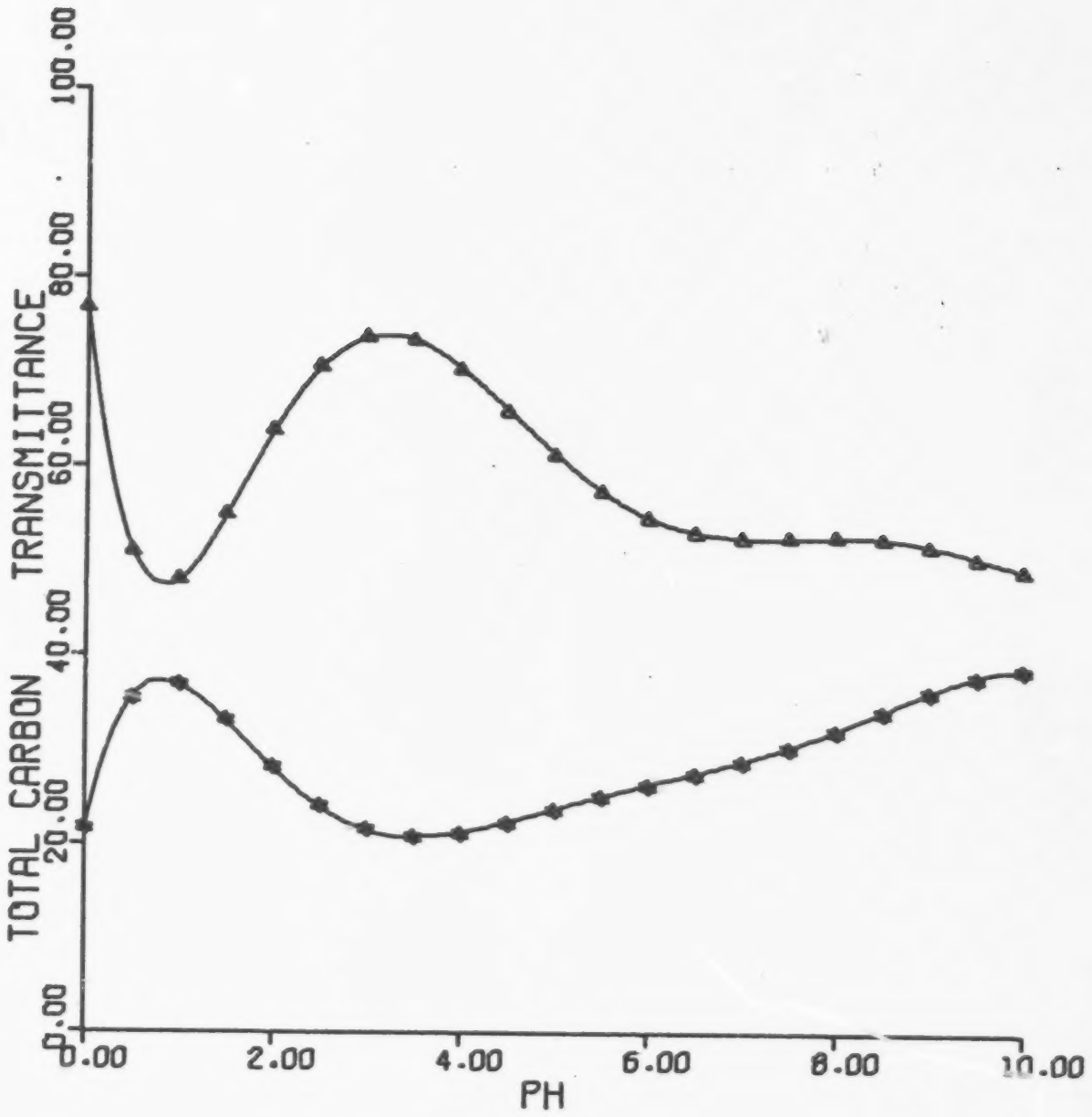


Figure 2

Δ Transmittance

* Total Carbon

ALUMINUM 60

CALCIUM 0

MAGNESIUM 0

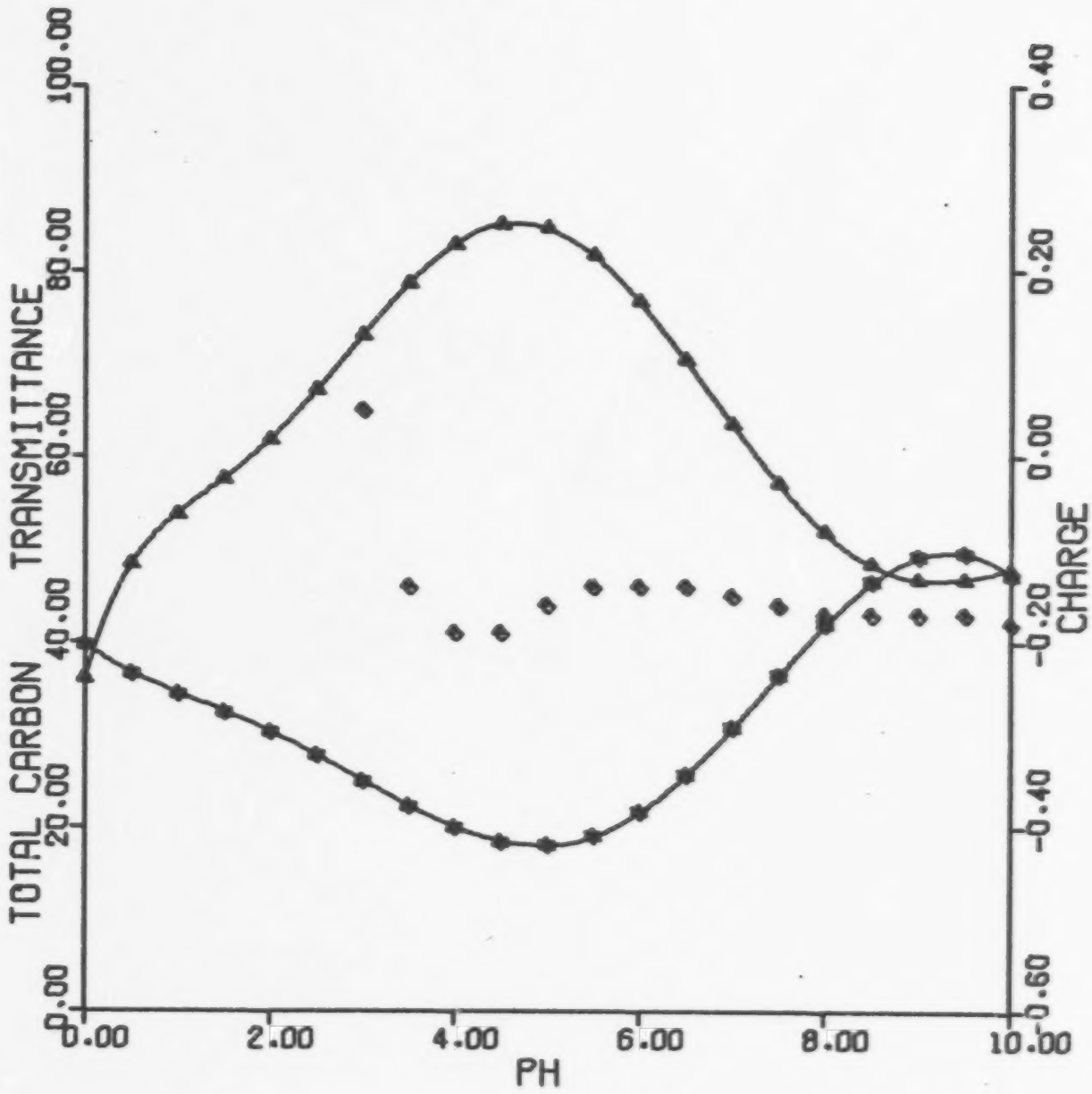


Figure 3

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 80

CALCIUM 0

MAGNESIUM 0

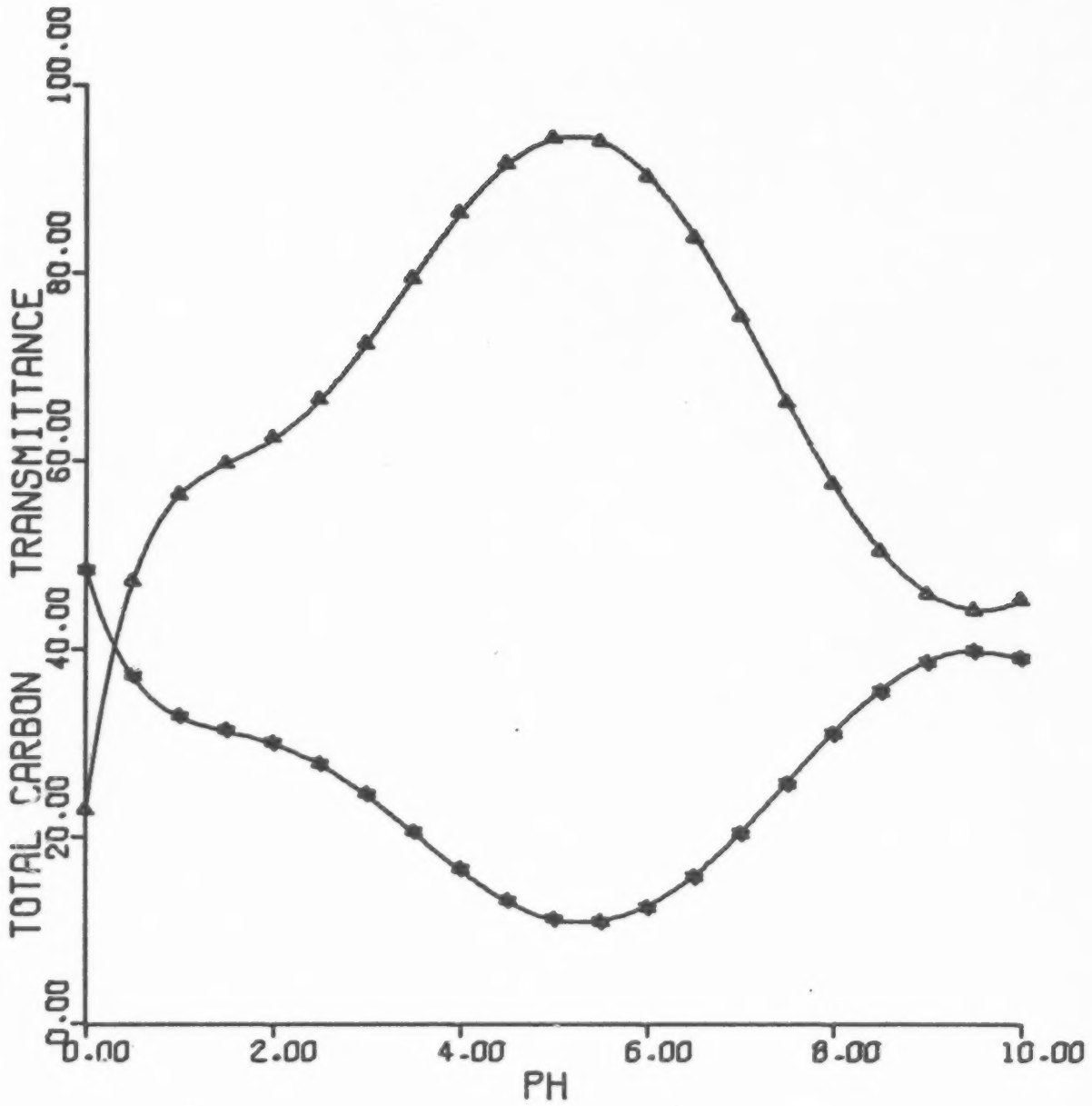


Figure 4

Δ Transmittance

* Total Carbon

ALUMINUM 100

CALCIUM 0

MAGNESIUM 0

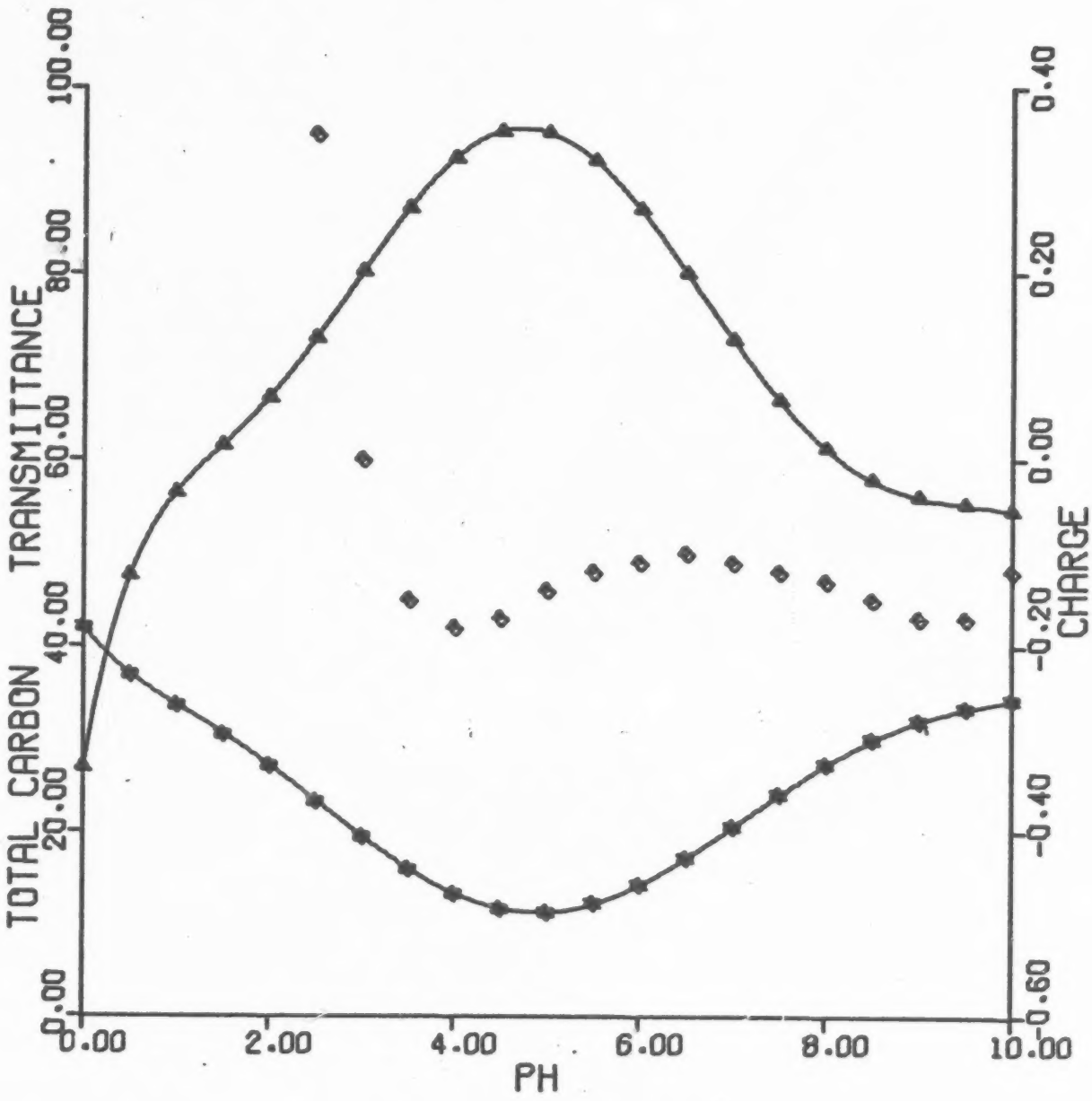


Figure 5

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 150

CALCIUM 0

MAGNESIUM 0

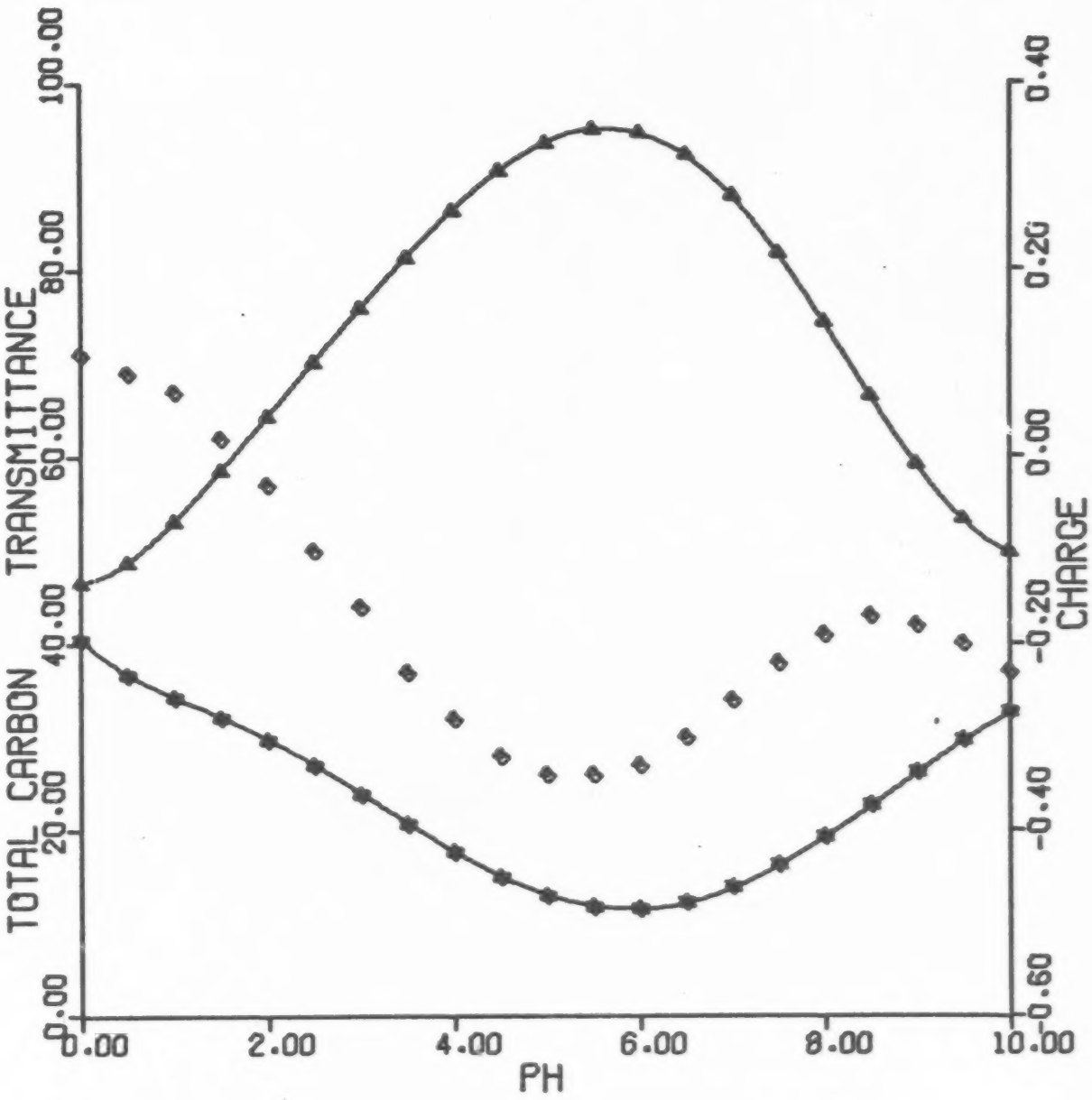
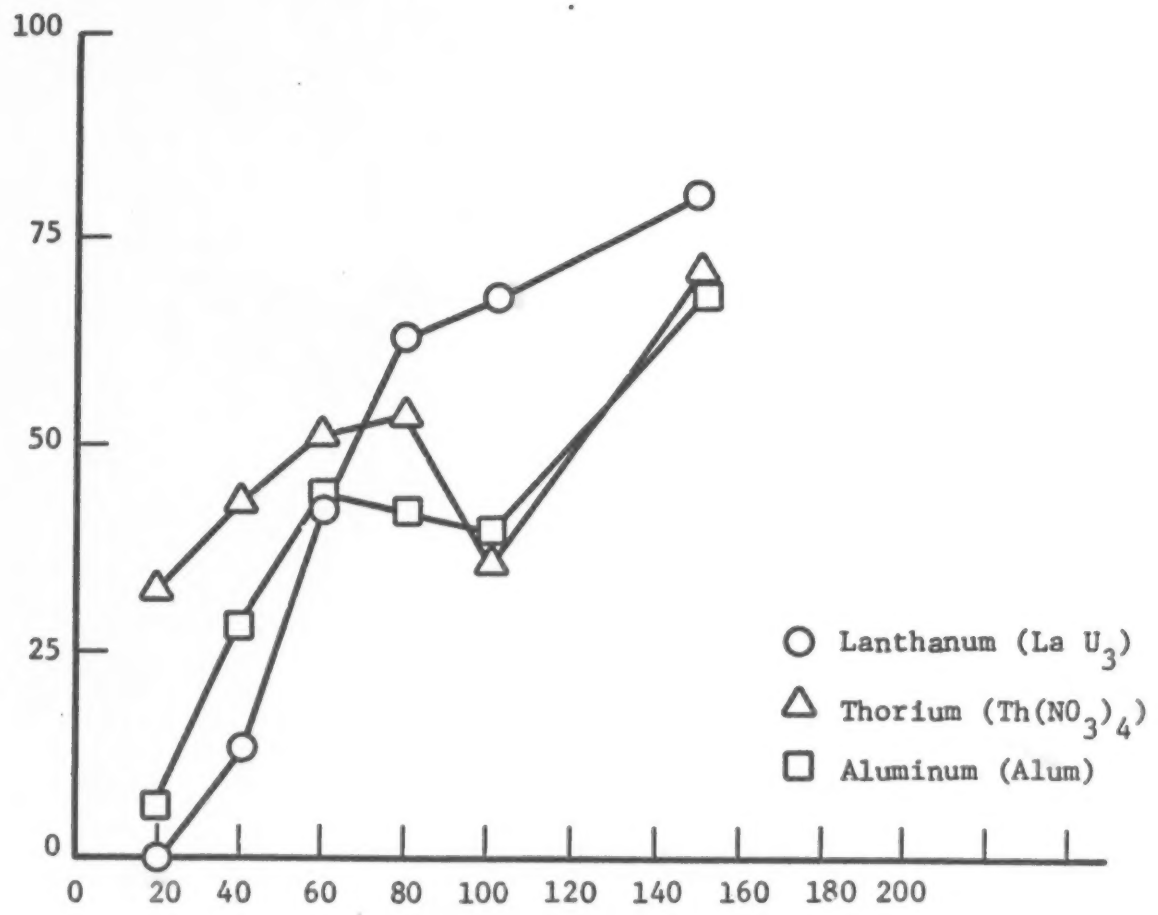


Figure 6

Δ Transmittance

■ Charge

* Total Carbon


Area sq cm
for %T > 60
100
75
50
25
0
0 20 40 60 80 100 120 140 160 180 200
Lanthanum (La U_3)
Thorium ($Th(NO_3)_4$)
Aluminum (Alum)

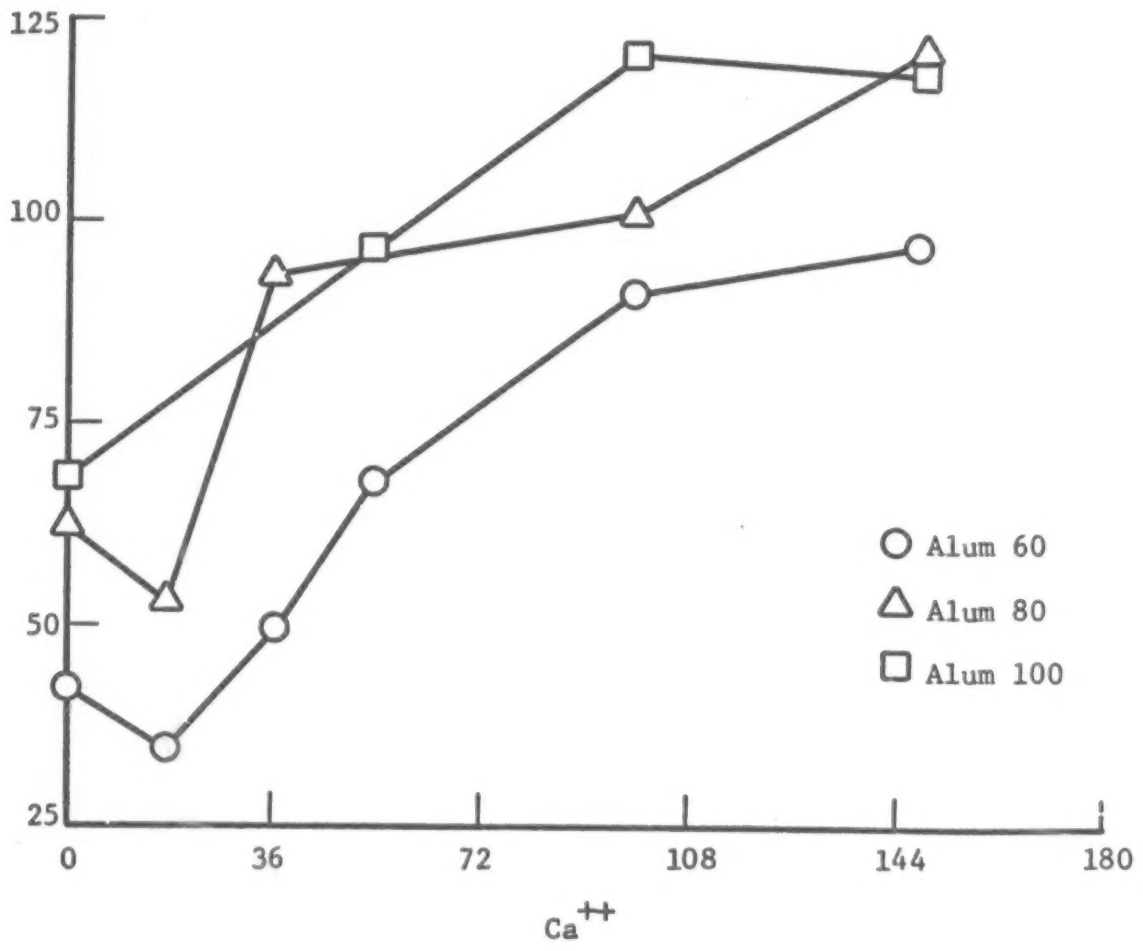

Area sq cm
for %T > 60
125
100
75
50
25
0 36 72 108 144 180
Ca^{++}
Alum 60
Alum 80
Alum 100

Figure 7

ALUMINUM 80

CALCIUM 150

MAGNESIUM 0

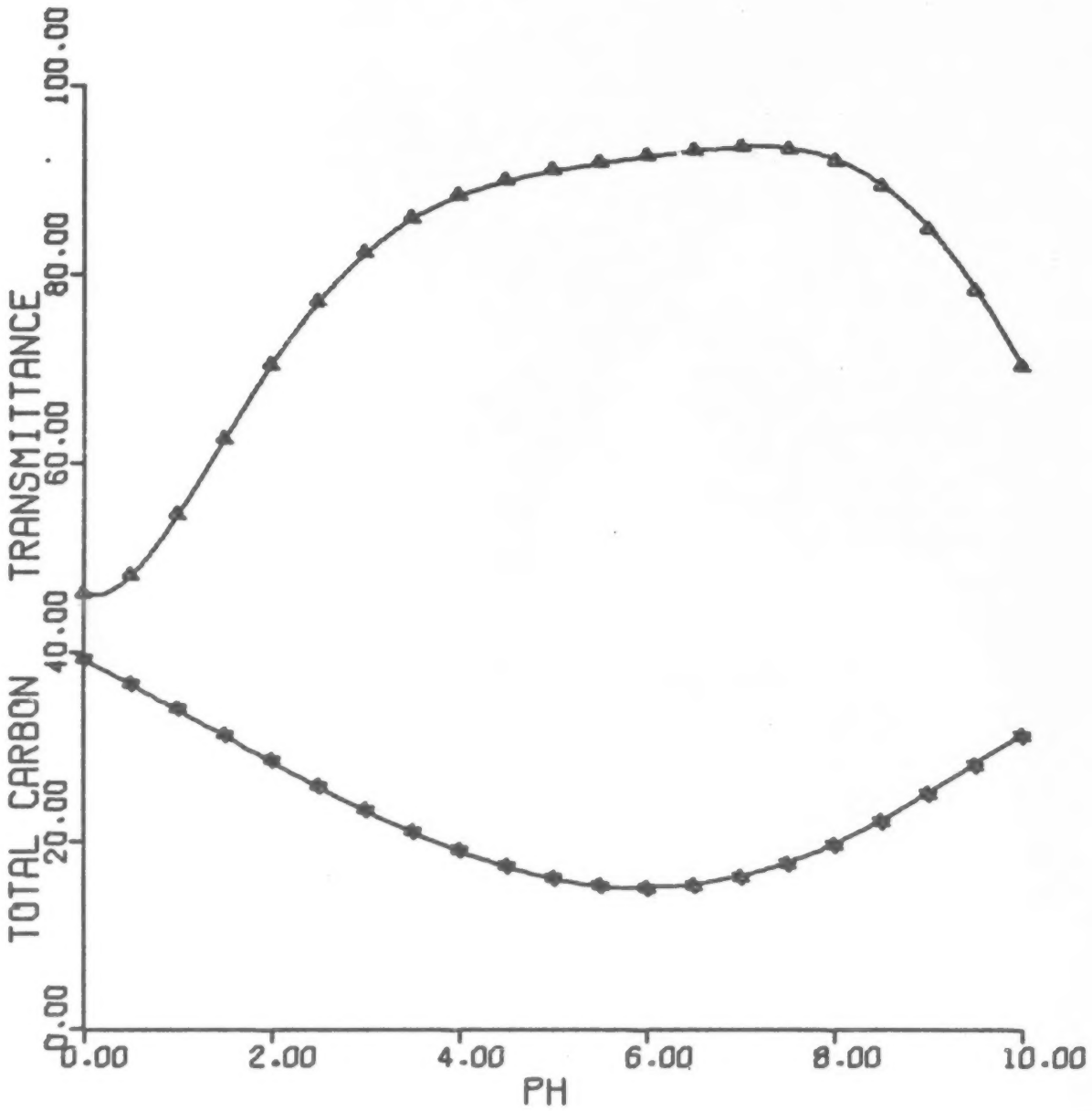


Figure 11

Δ Transmittance

* Total Carbon

ALUMINUM 80

CALCIUM 100

MAGNESIUM 0

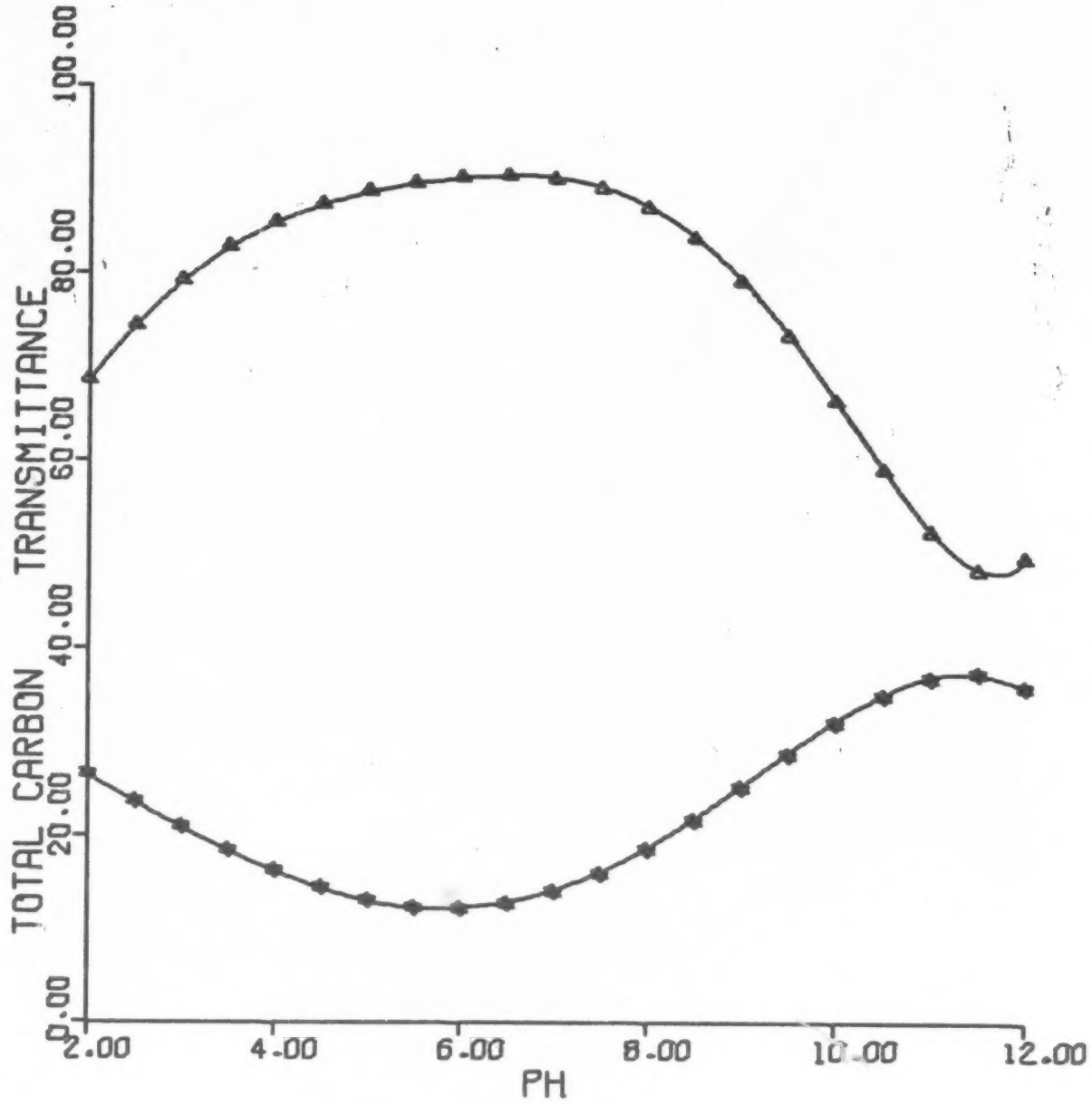


Figure 10

Δ Transmittance

* Total Carbon

ALUMINUM 80

CALCIUM 37

MAGNESIUM 0

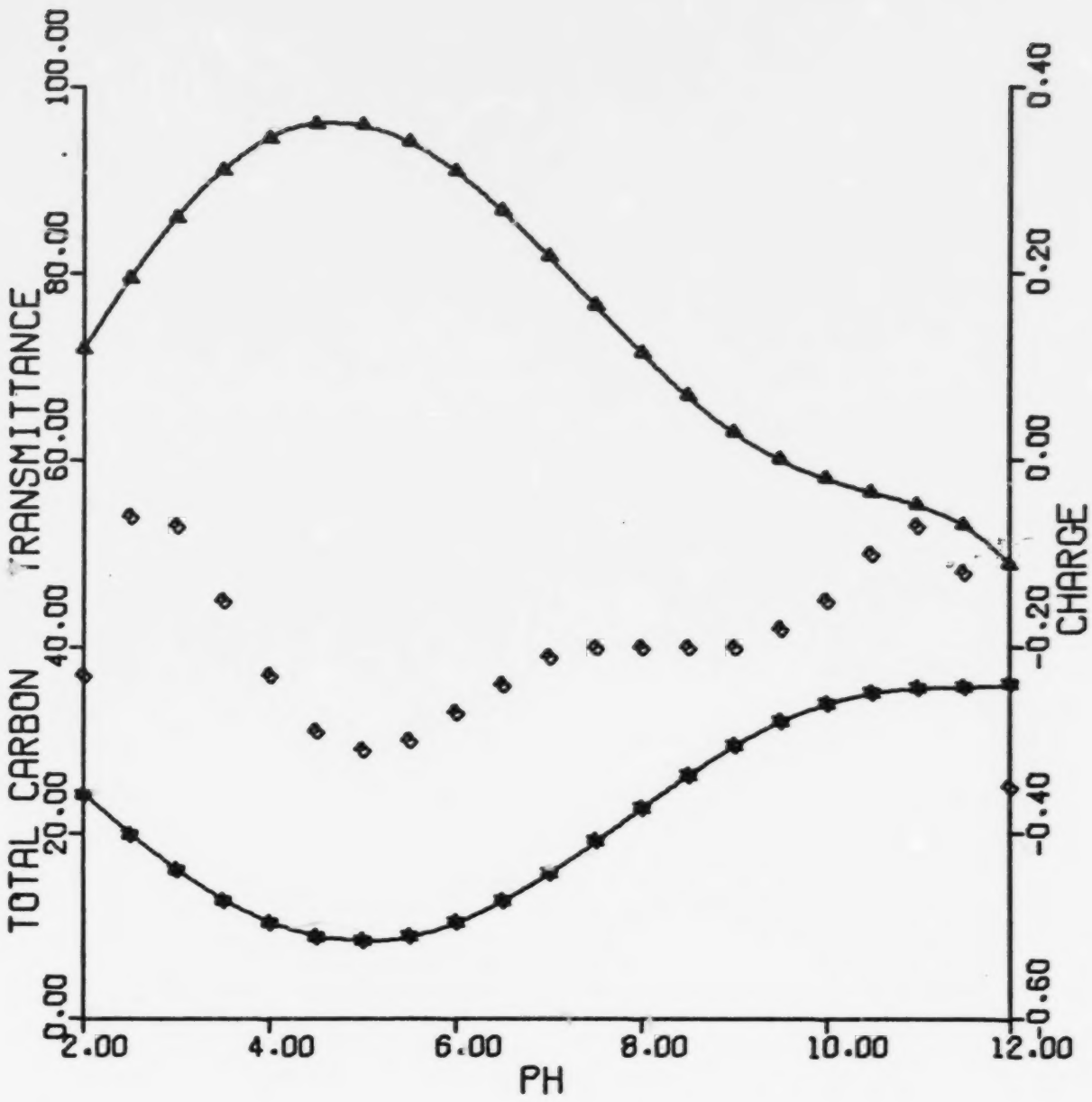


Figure 9

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 80

CALCIUM 18

MAGNESIUM 0

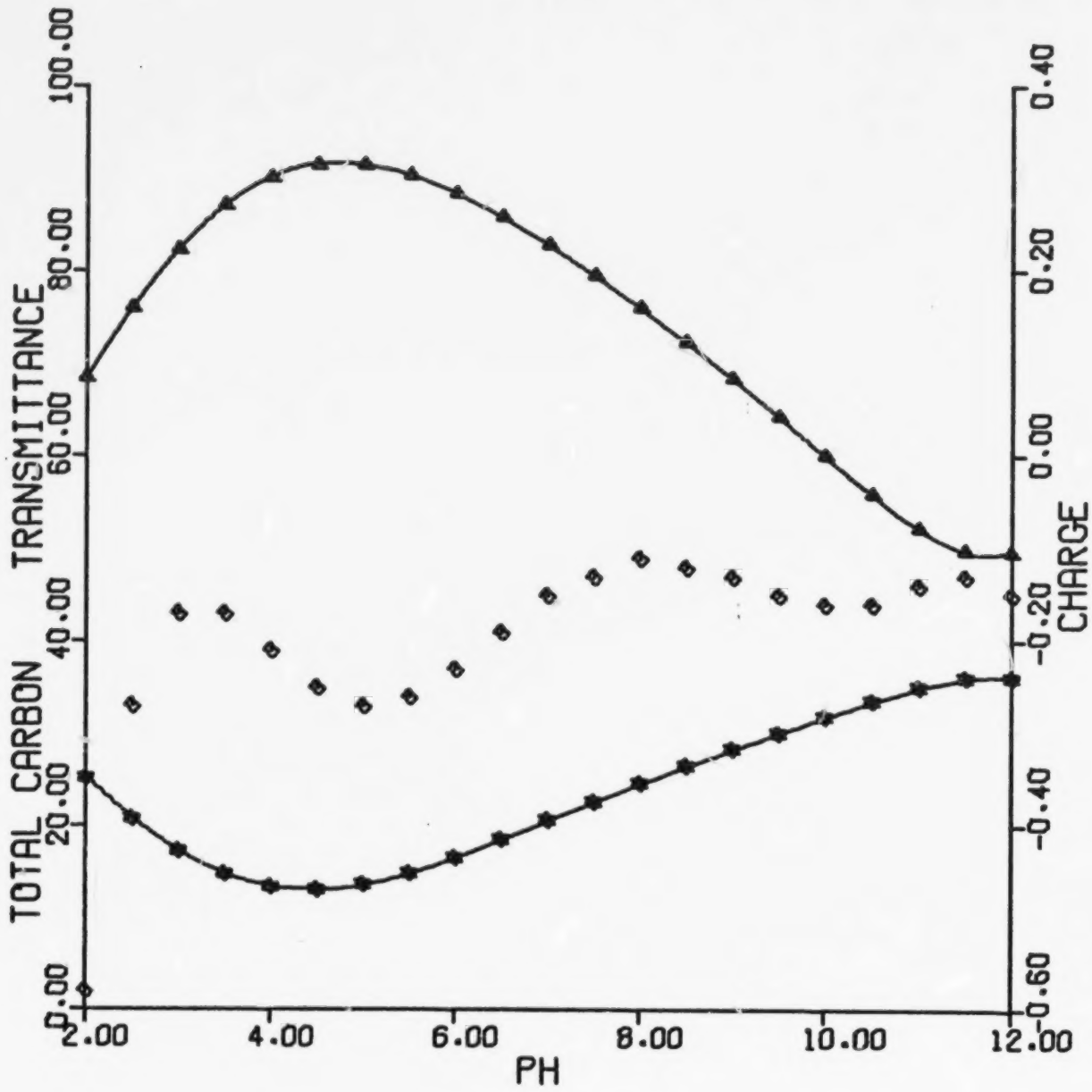


Figure 8

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 40

CALCIUM 0

MAGNESIUM 13

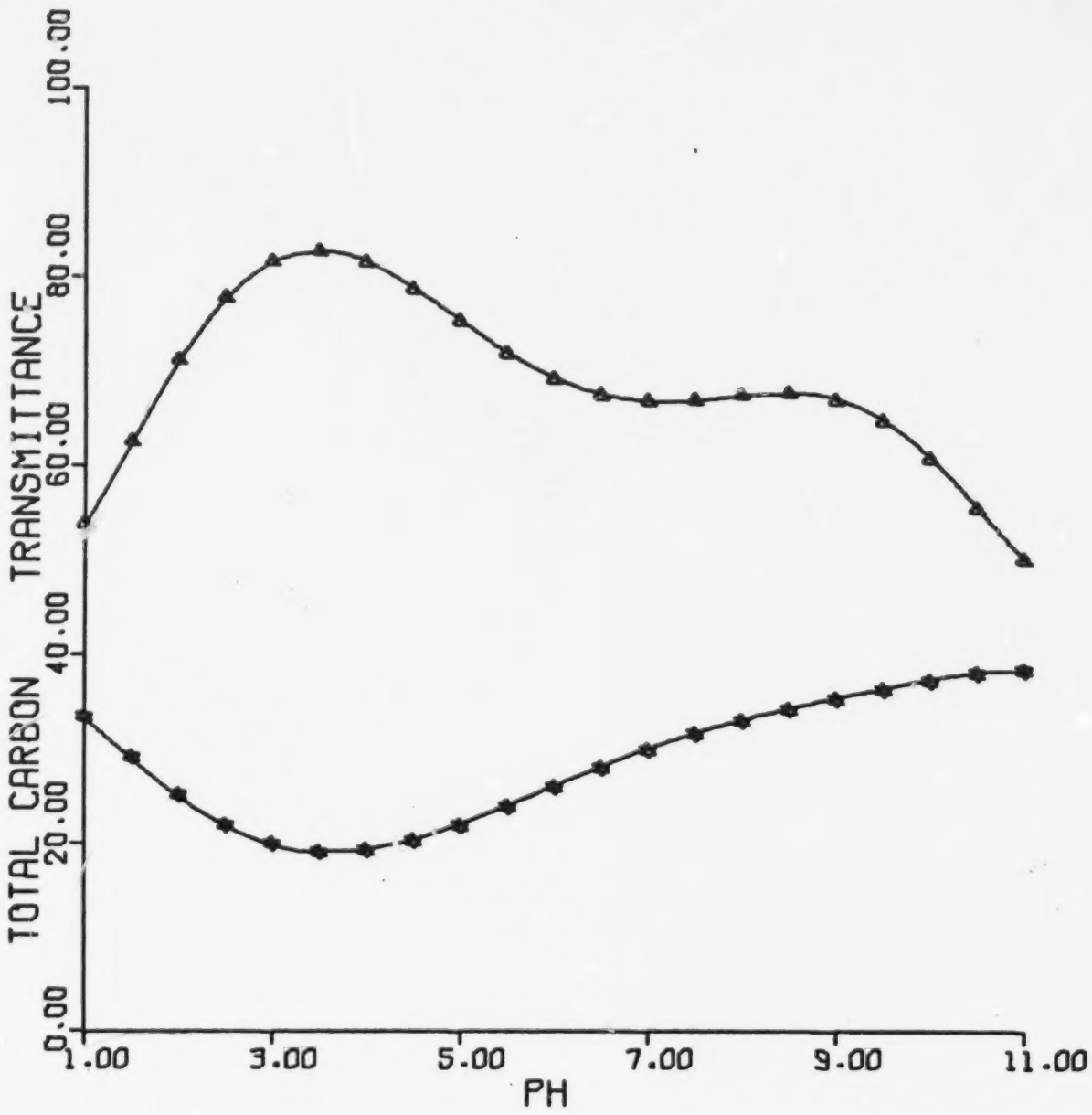


Figure 12

Δ Transmittance

* Total Carbon

ALUMINUM 40

CALCIUM 0

MAGNESIUM 26

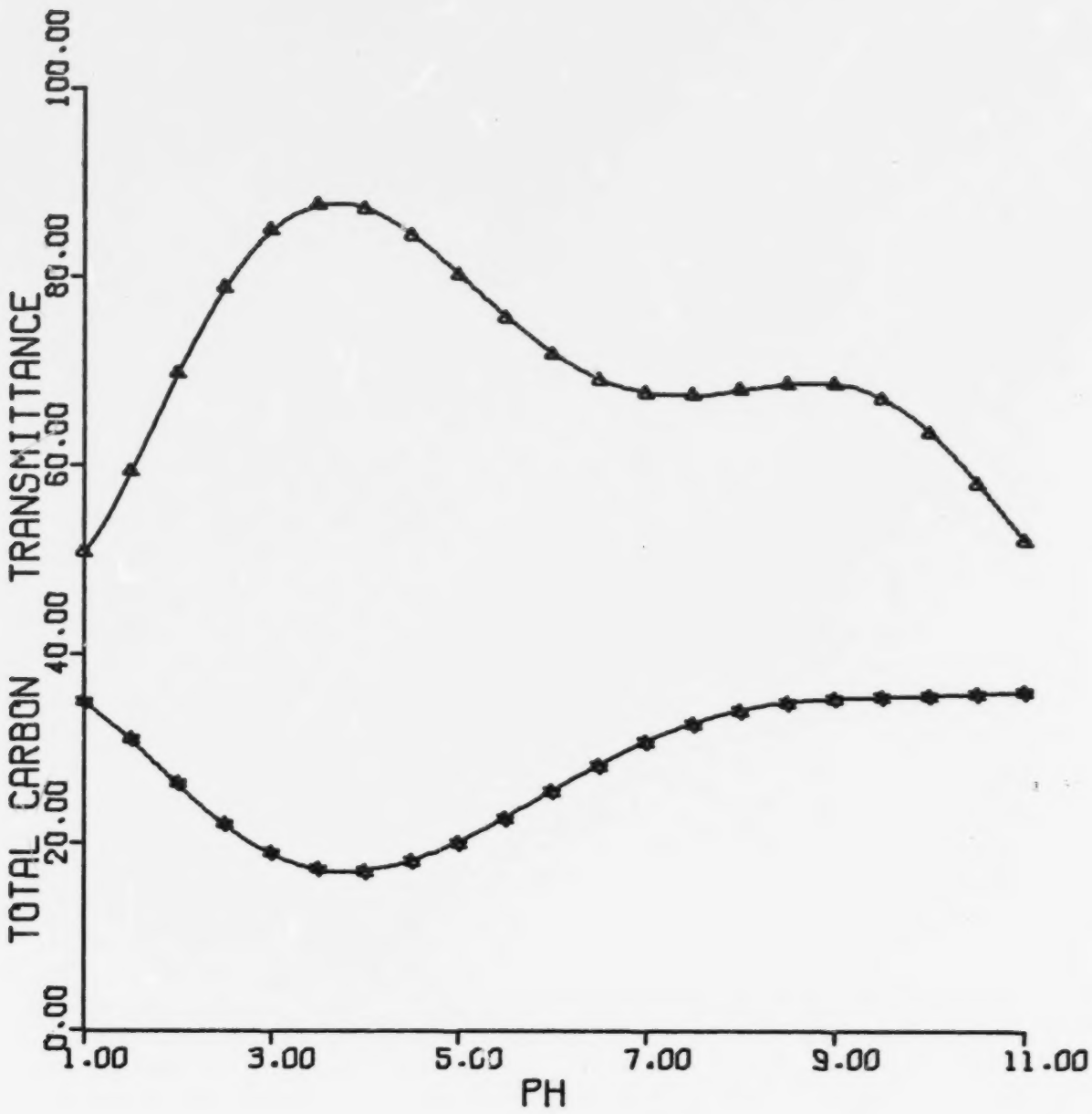


Figure 13

Δ Transmittance

* Total Carbon

ALUMINUM 60

CALCIUM 0

MAGNESIUM 13

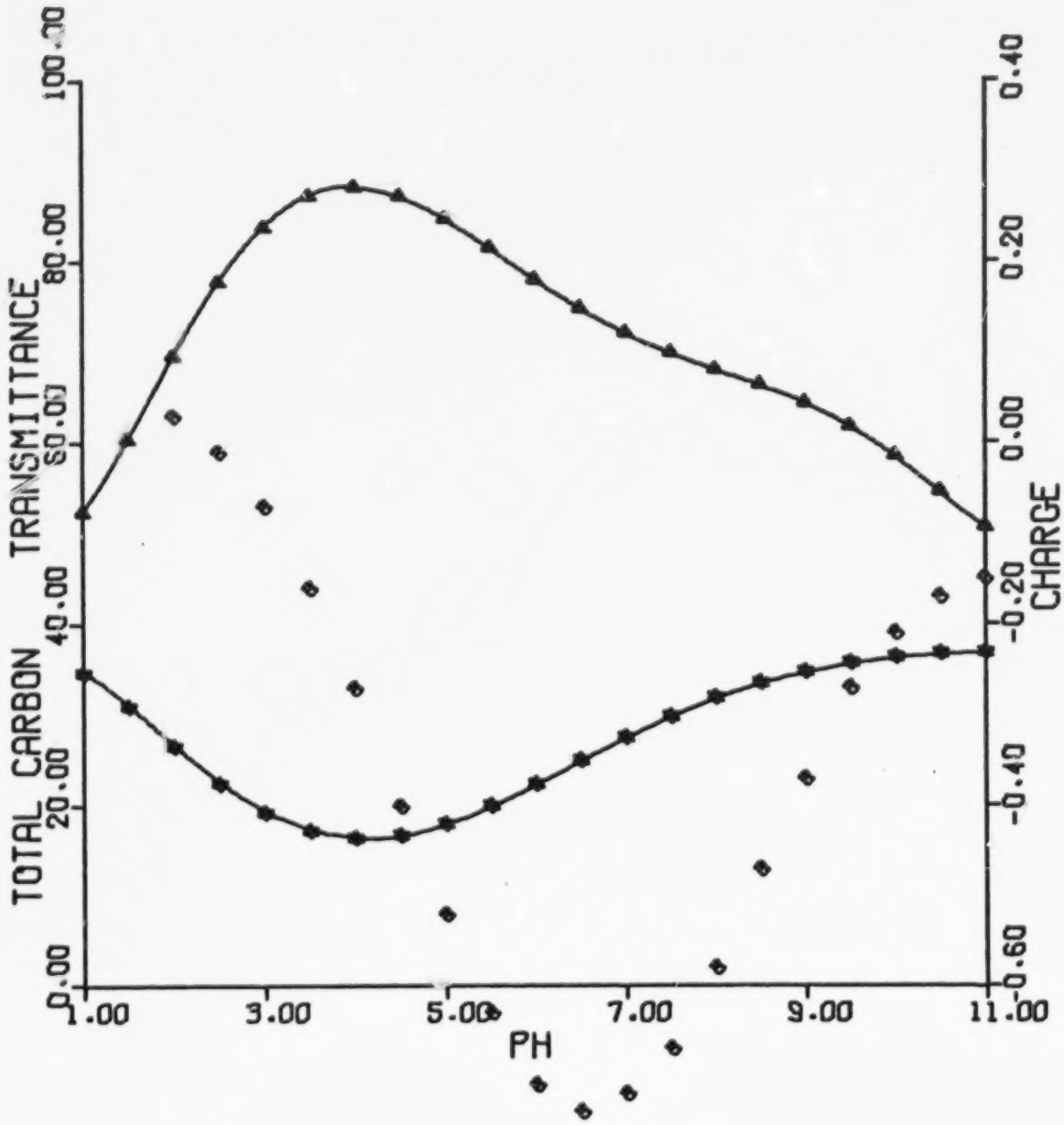


Figure 14

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 60

CALCIUM 0

MAGNESIUM 26

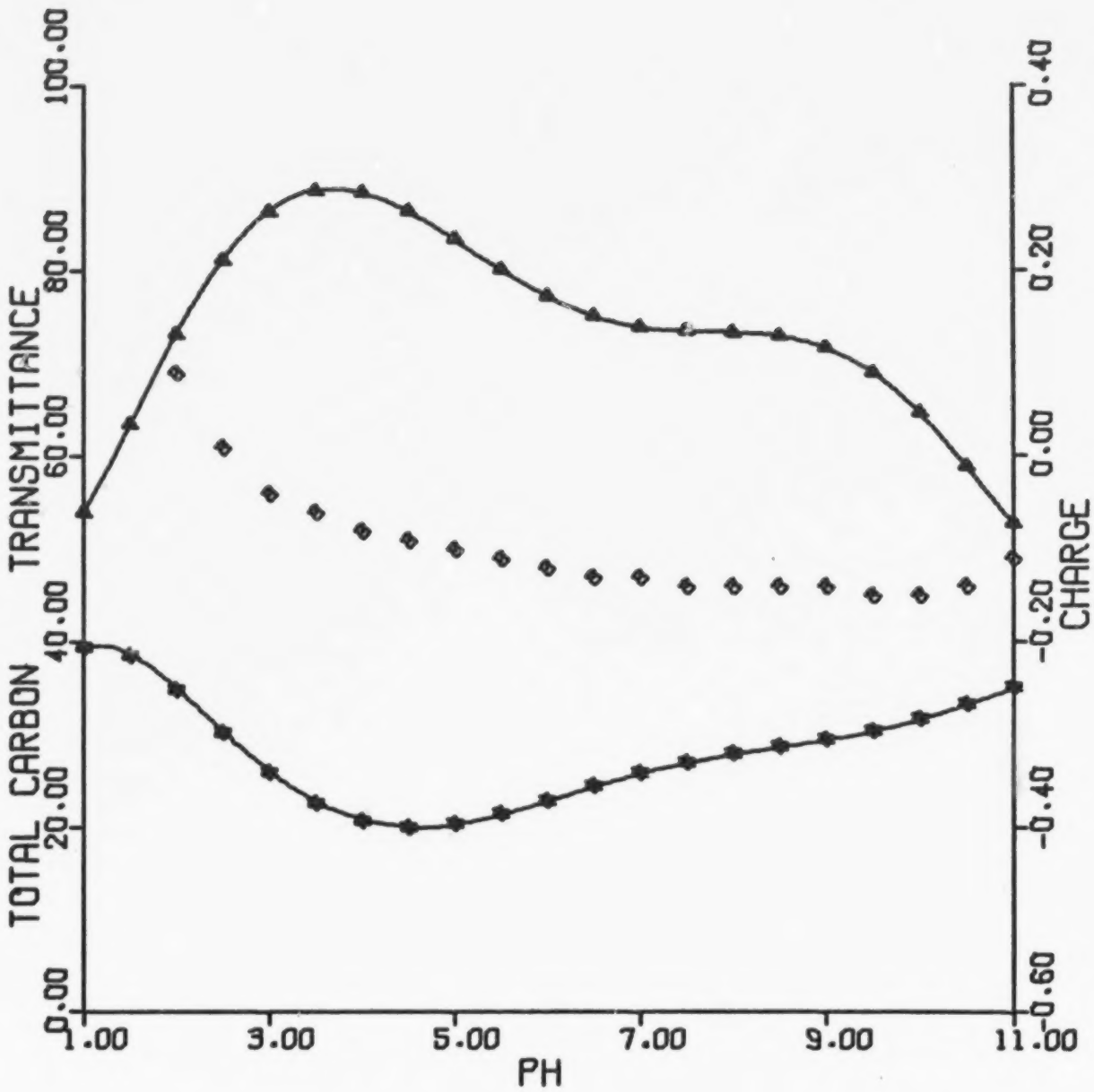


Figure 15

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 60

CALCIUM 9

MAGNESIUM 6

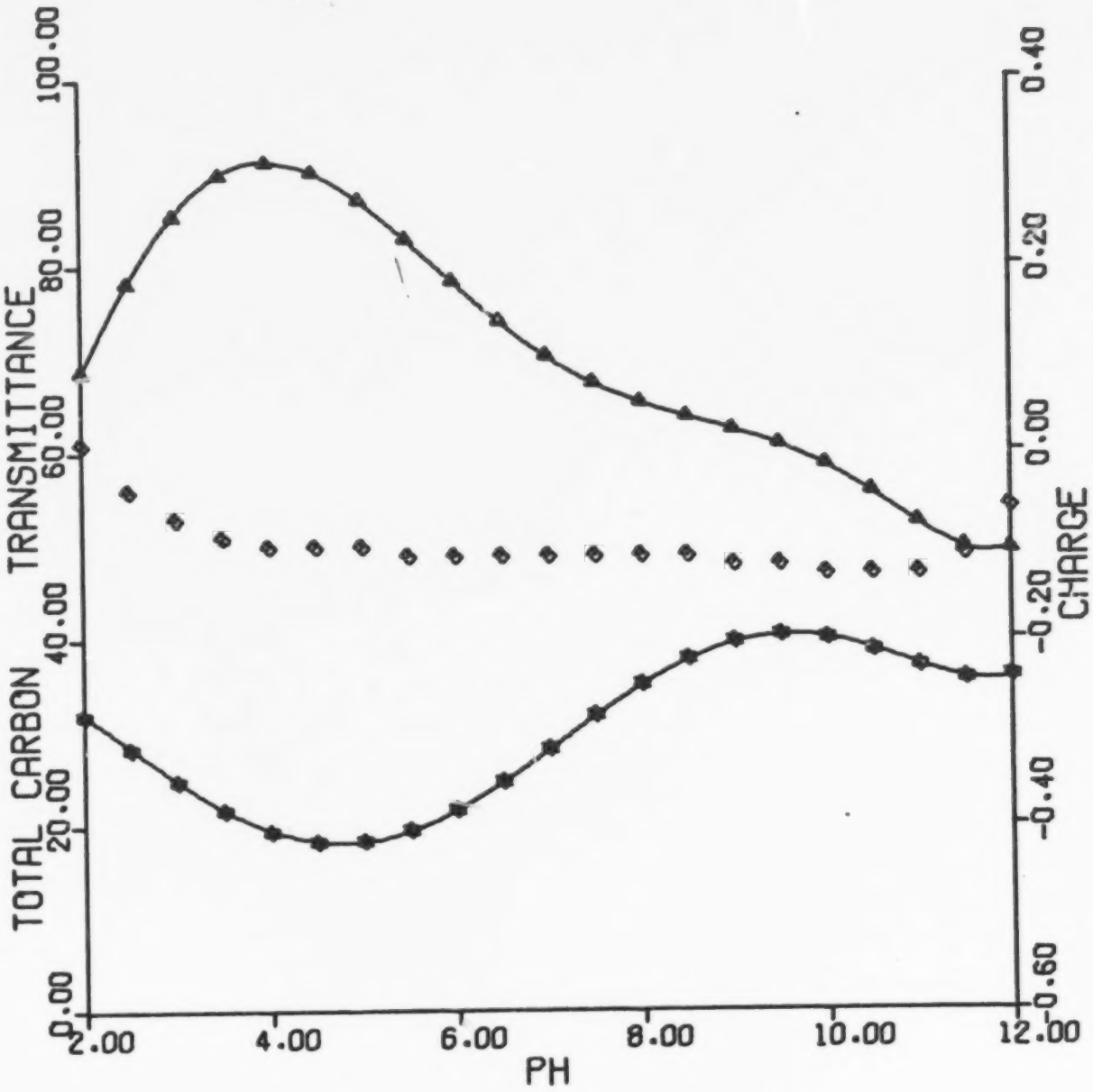


Figure 16

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 60

CALCIUM 9

MAGNESIUM 13

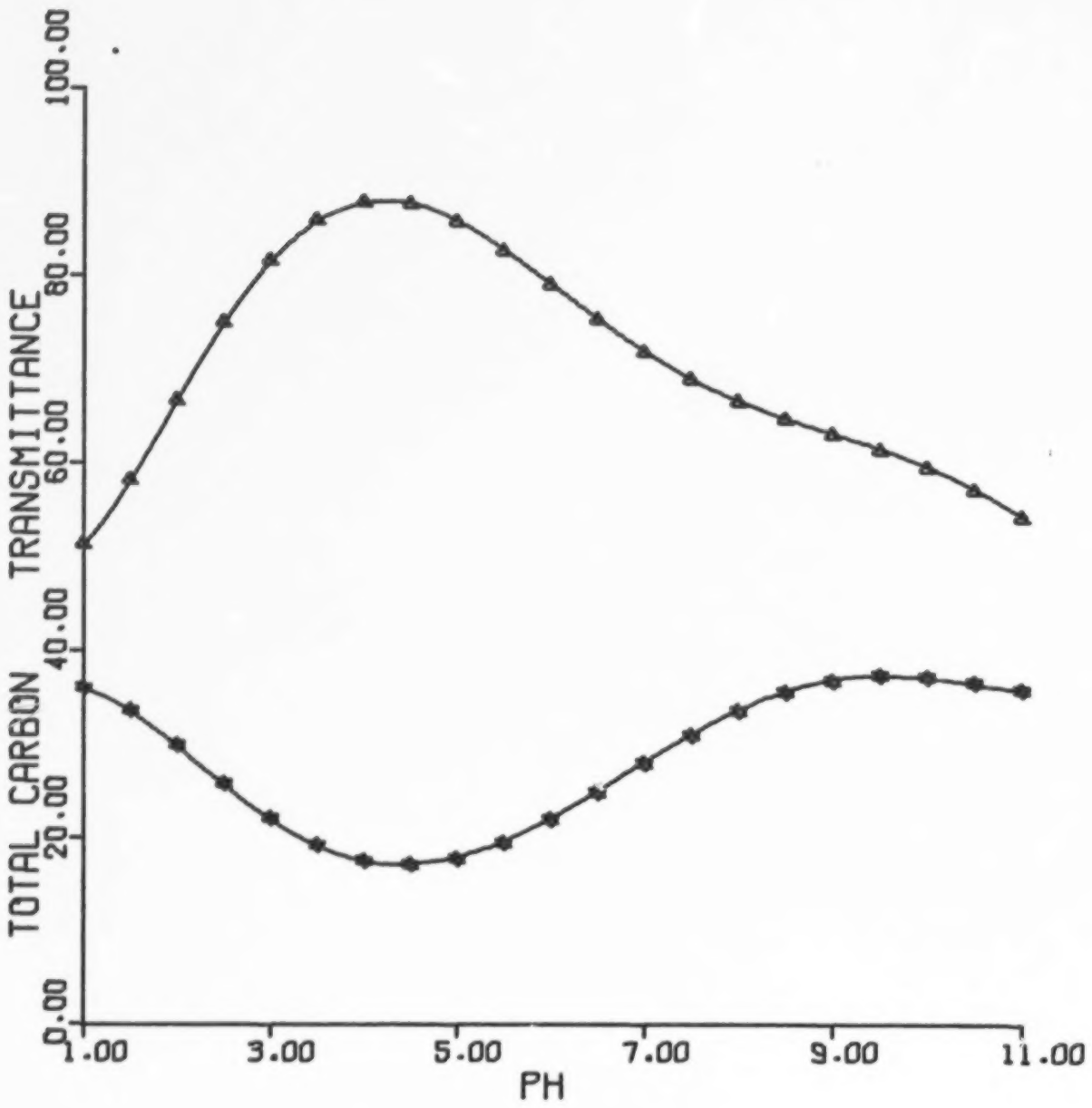


Figure 17

Δ Transmittance

* Total Carbon

ALUMINUM 60

CALCIUM 18

MAGNESIUM 6

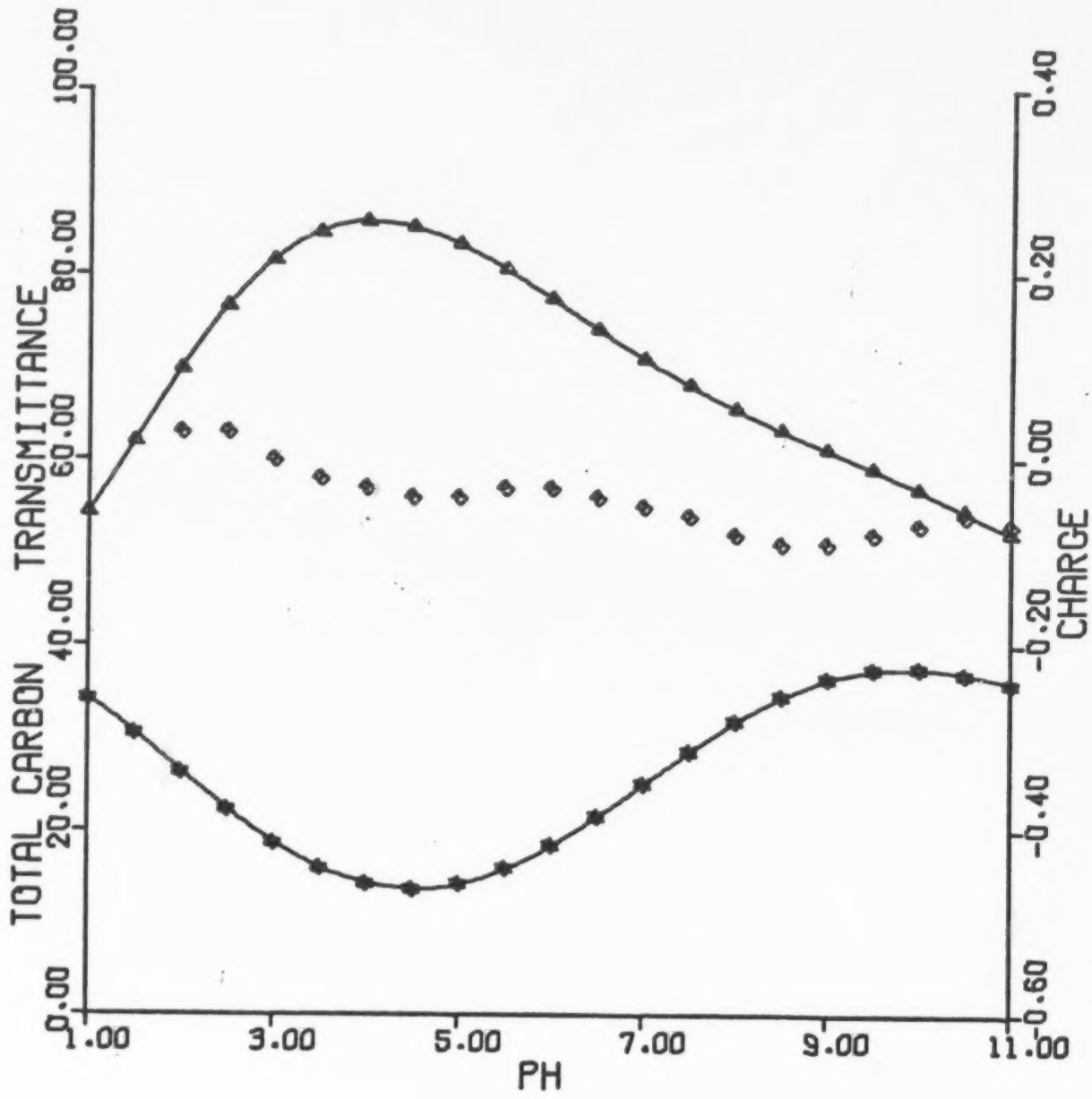


Figure 18

Δ Transmittance

■ Charge

* Total Carbon

ALUMINUM 60

CALCIUM 18

MAGNESIUM 13

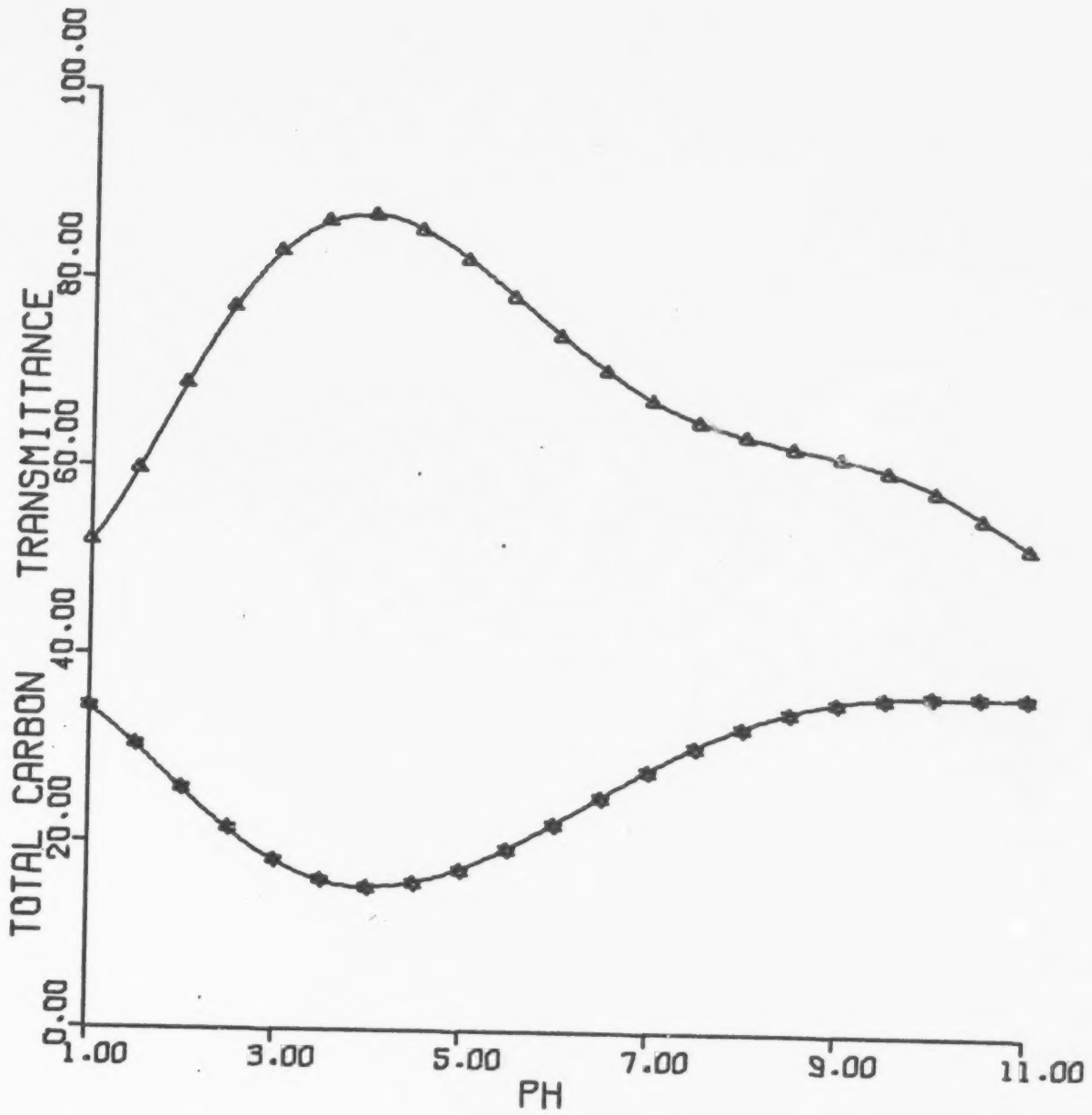


Figure 19

Δ Transmittance

* Total Carbon

LANTHANUM 20

CALCIUM 0

MAGNESIUM 0

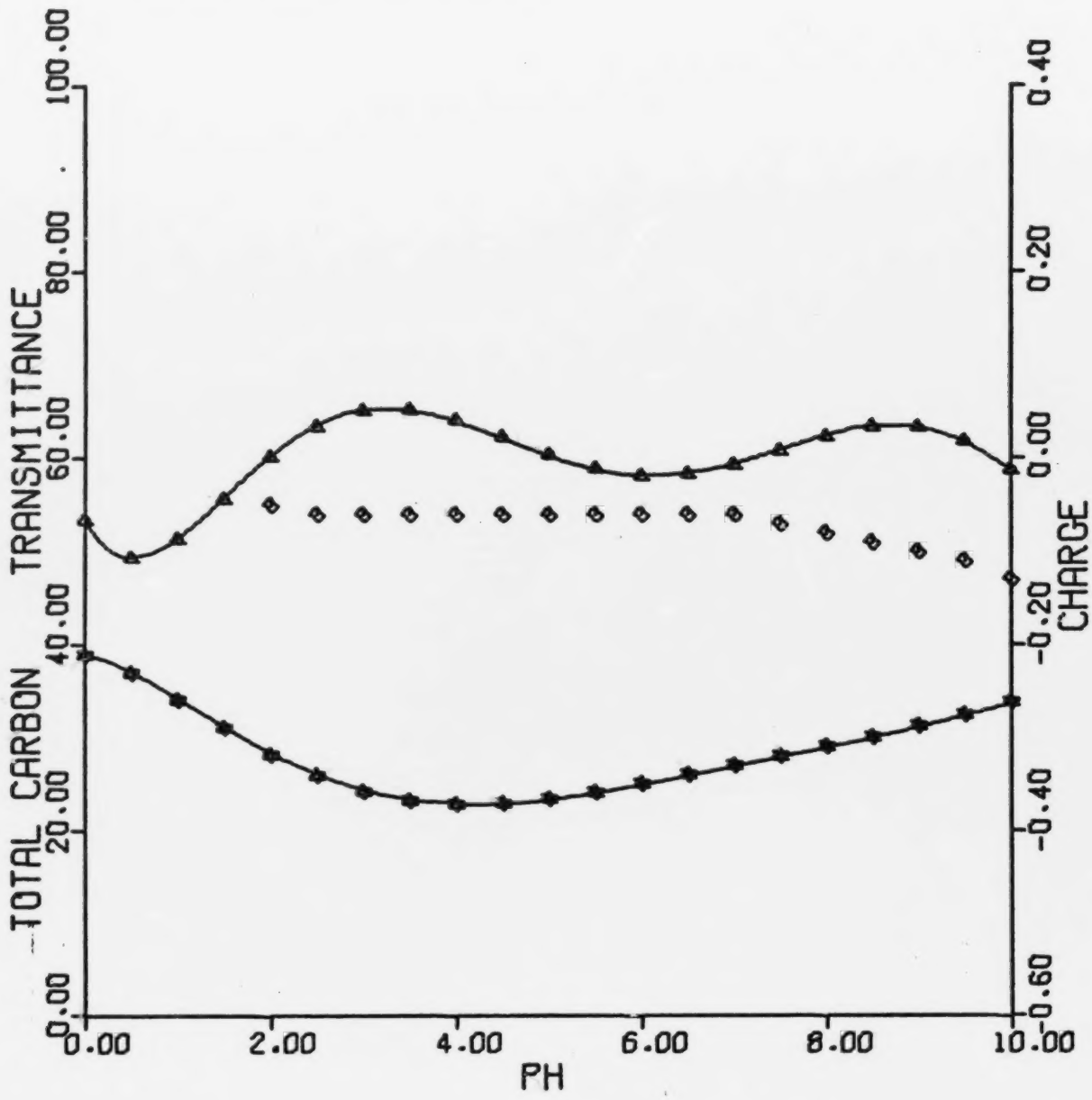


Figure 20

Δ Transmittance

■ Charge

* Total Carbon

LANTHANUM 40

CALCIUM 0

MAGNESIUM 0

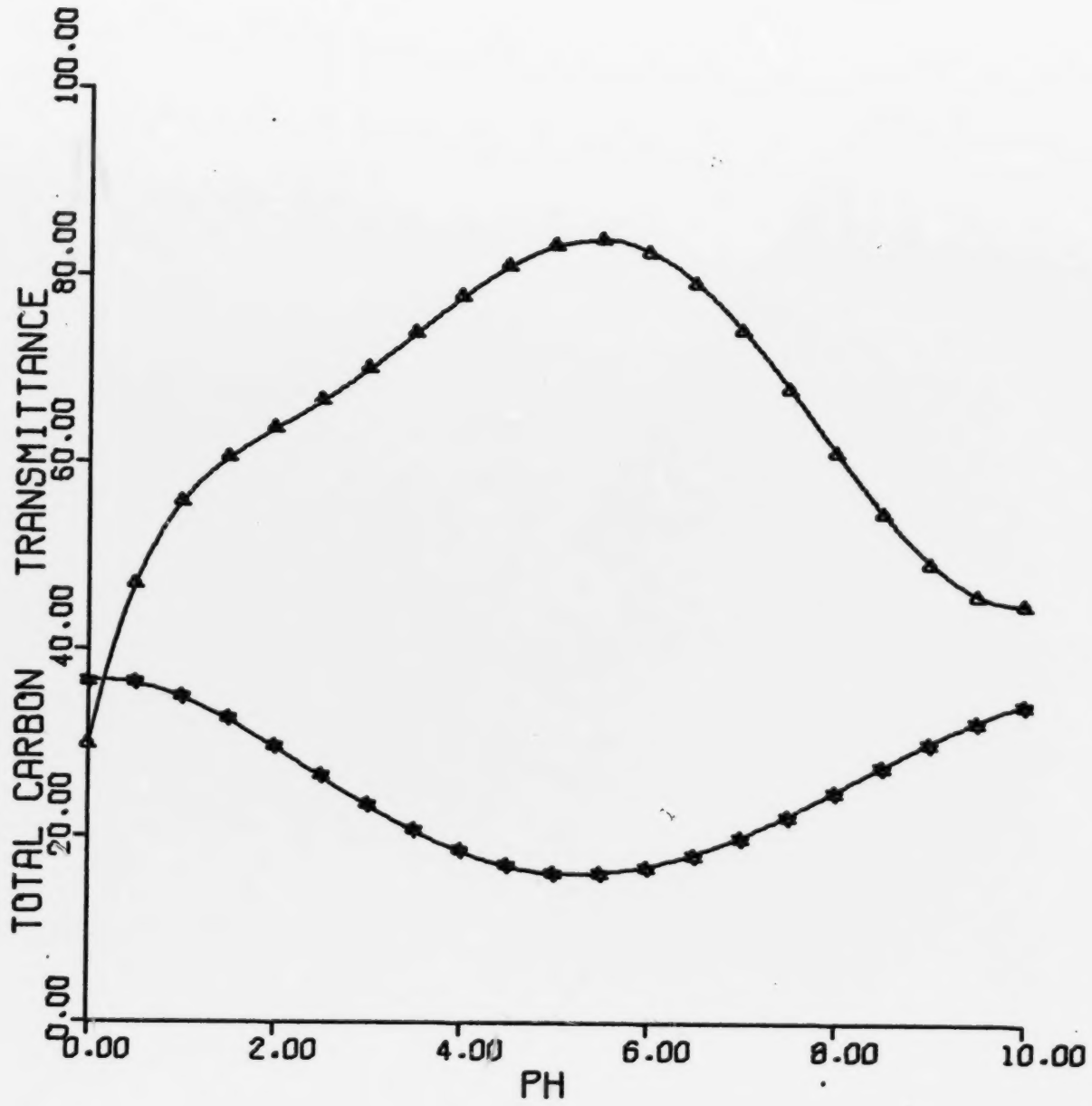


Figure 21

Δ Transmittance

* Total Carbon

LANTHANUM 60

CALCIUM 0

MAGNESIUM 0

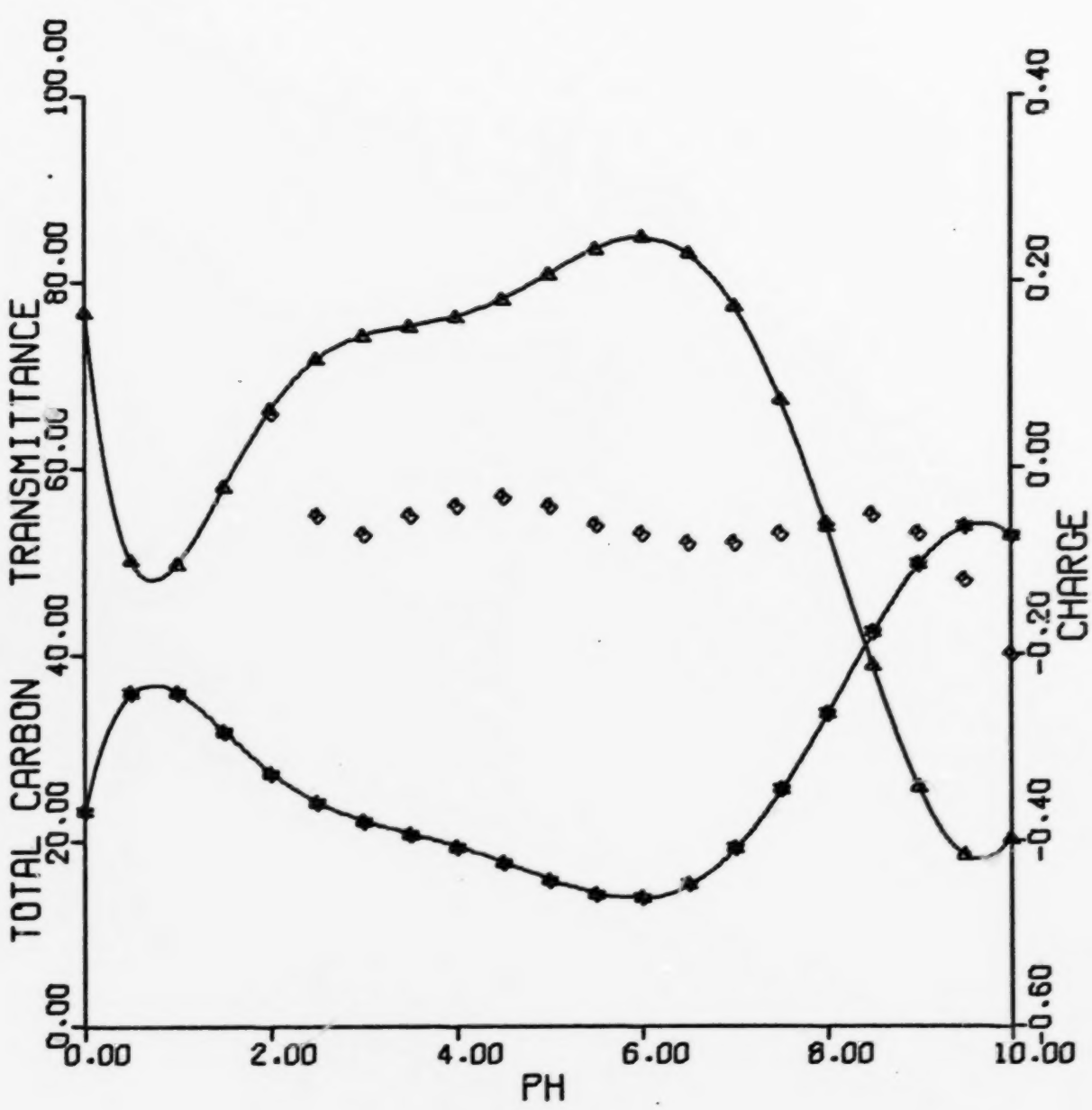


Figure 22

Δ Transmittance

■ Charge

* Total Carbon

LANTHANUM 80

CALCIUM 0

MAGNESIUM 0

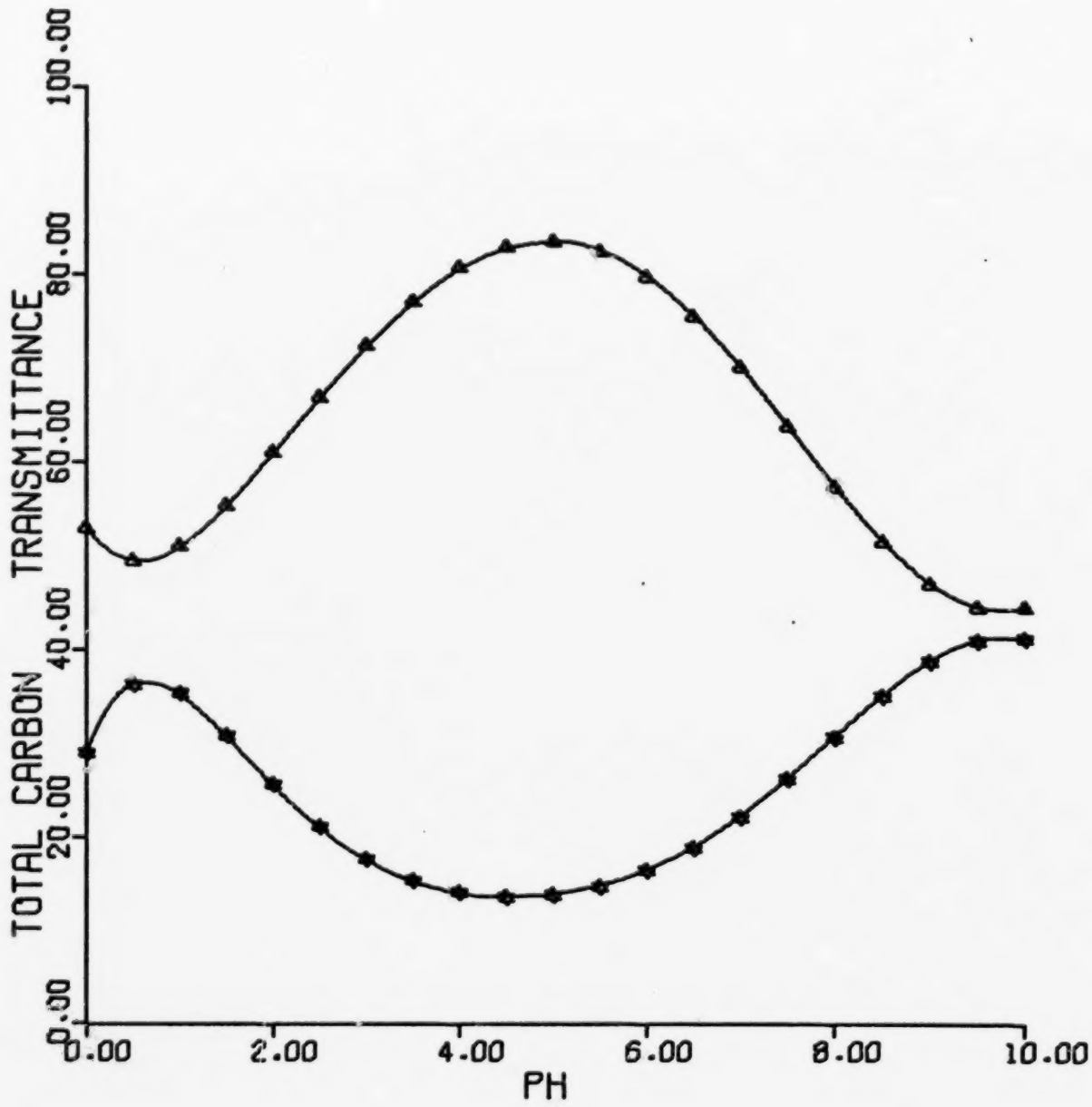


Figure 23

Δ Transmittance

* Total Carbon

LANTHANUM 100

CALCIUM 0

MAGNESIUM 0

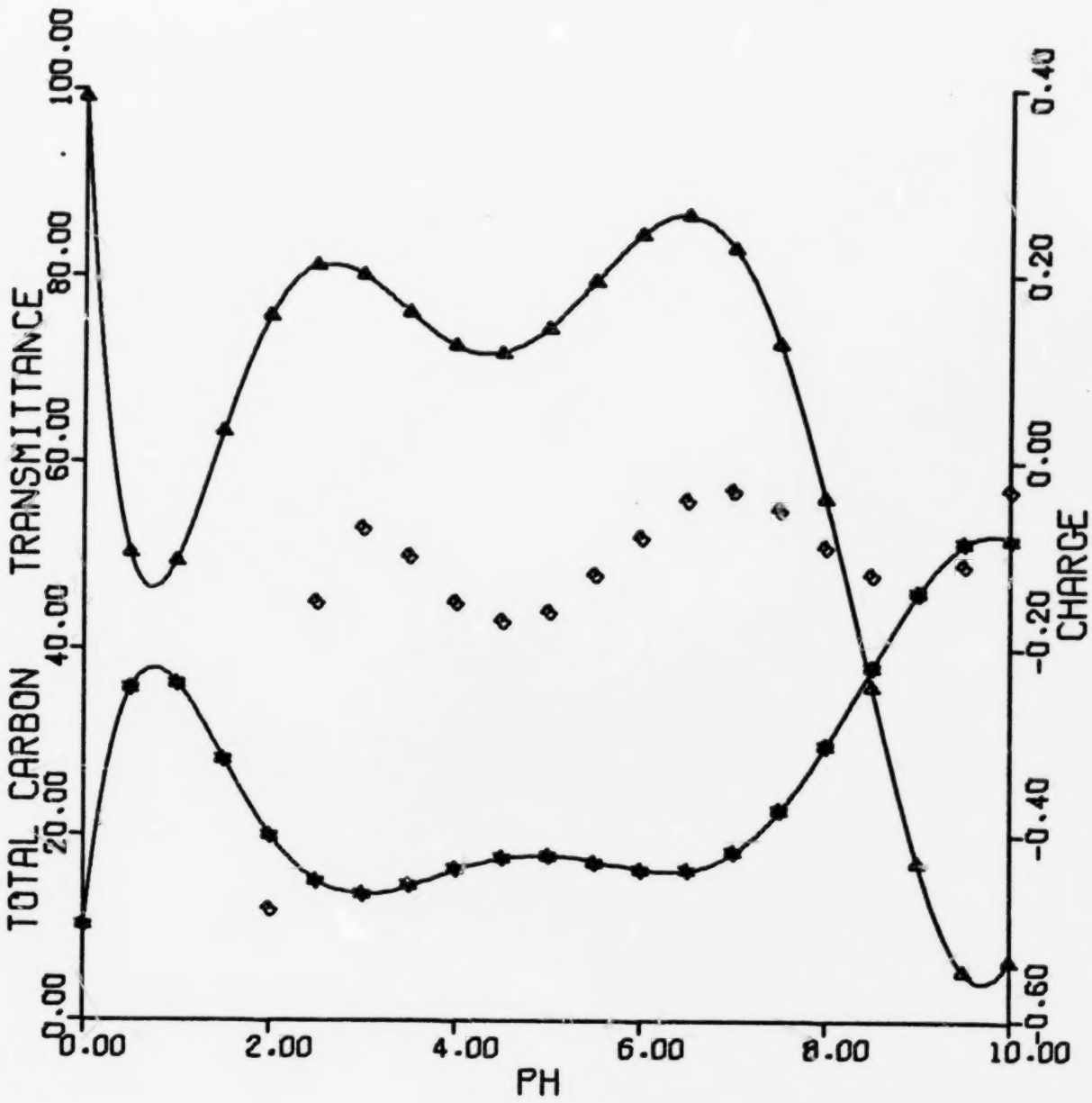


Figure 24

Δ Transmittance

■ Charge

* Total Carbon

LANTHANUM 150

CALCIUM 0

MAGNESIUM 0

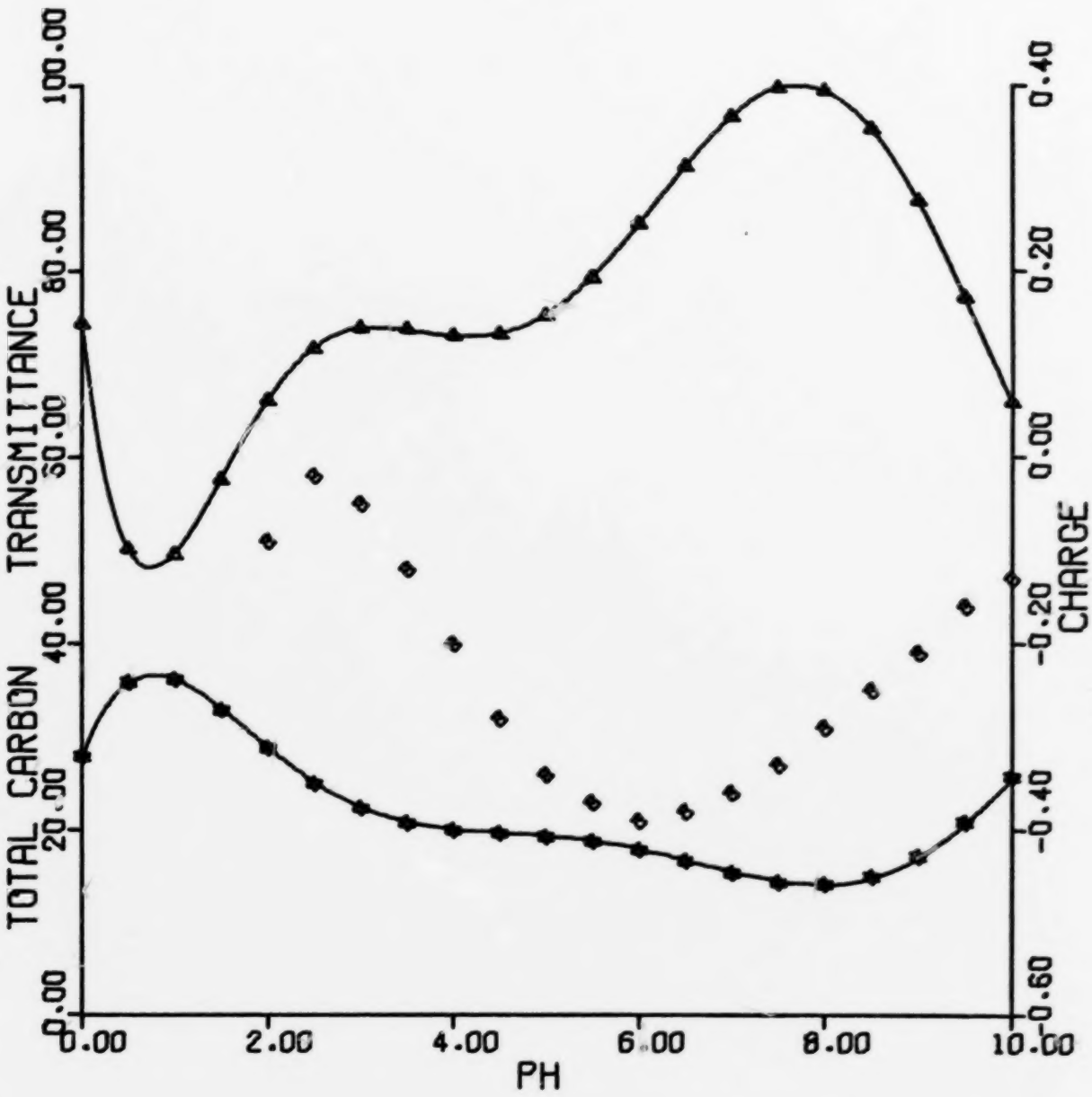


Figure 25

Δ Transmittance

■ Charge

* Total Carbon

LANTHANUM 60

CALCIUM 18

MAGNESIUM 0

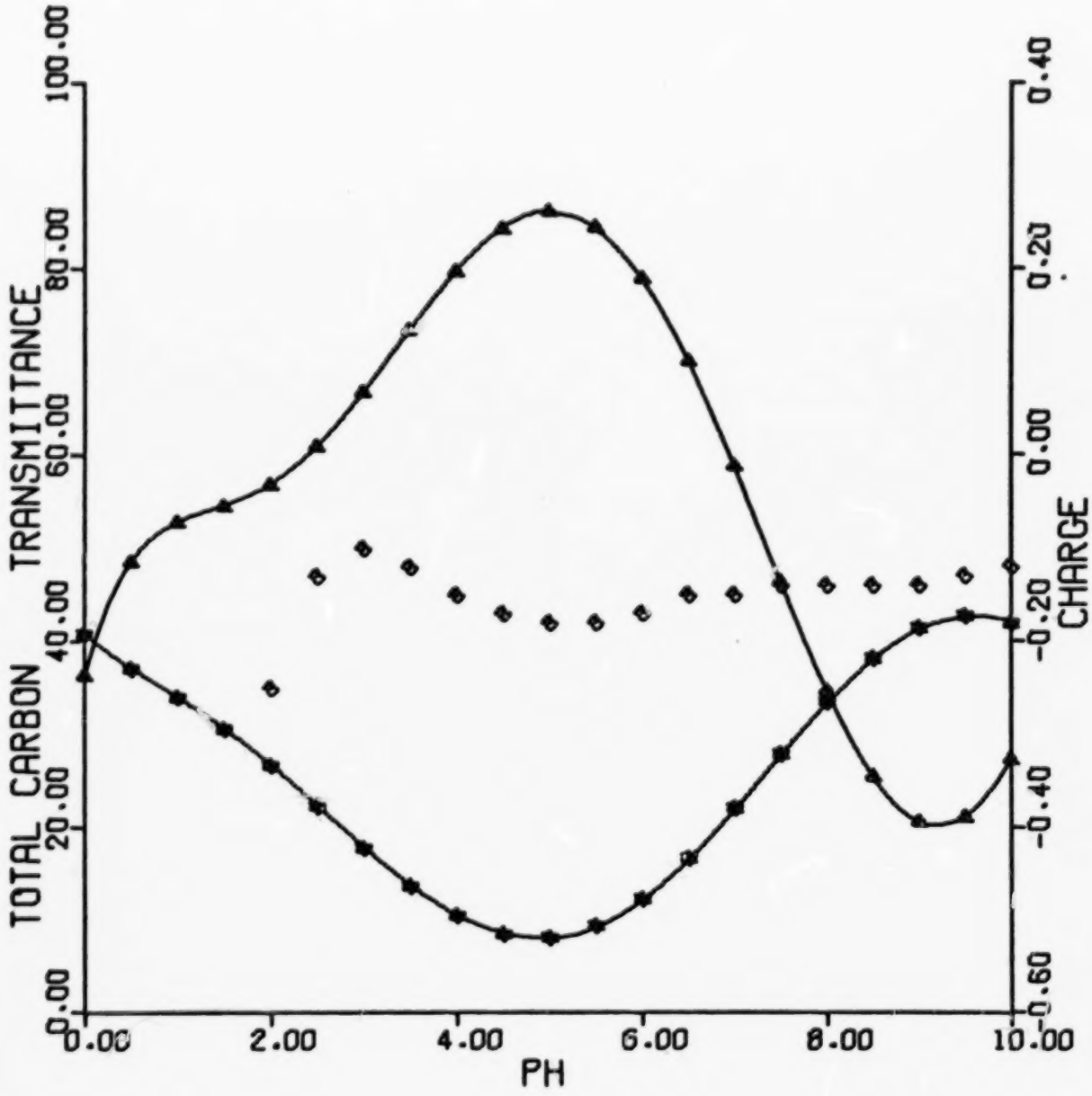


Figure 26

Δ Transmittance

■ Charge

* Total Carbon

LANTHANUM 60

CALCIUM 37

MAGNESIUM 0

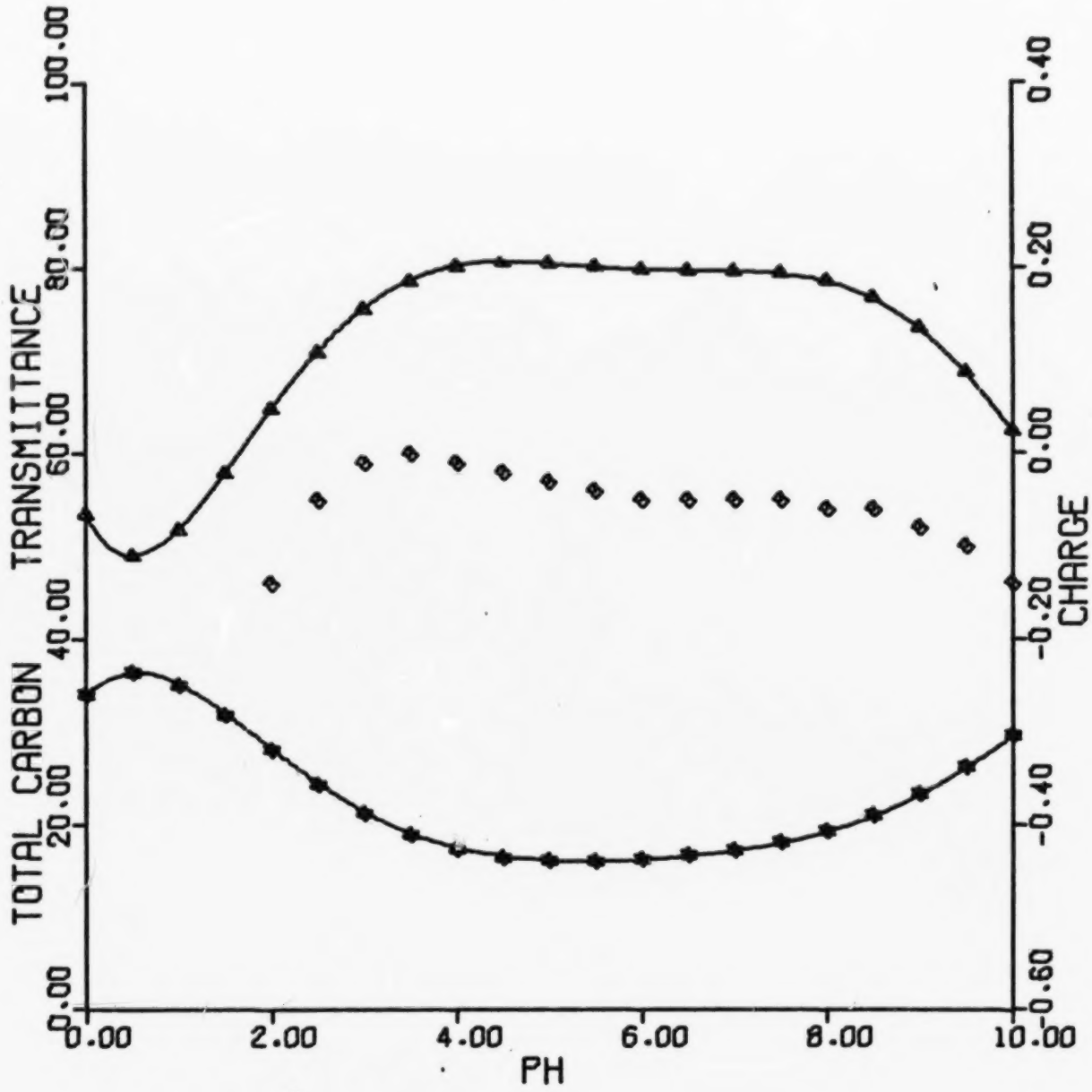


Figure 27

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 20

CALCIUM 0

MAGNESIUM 0

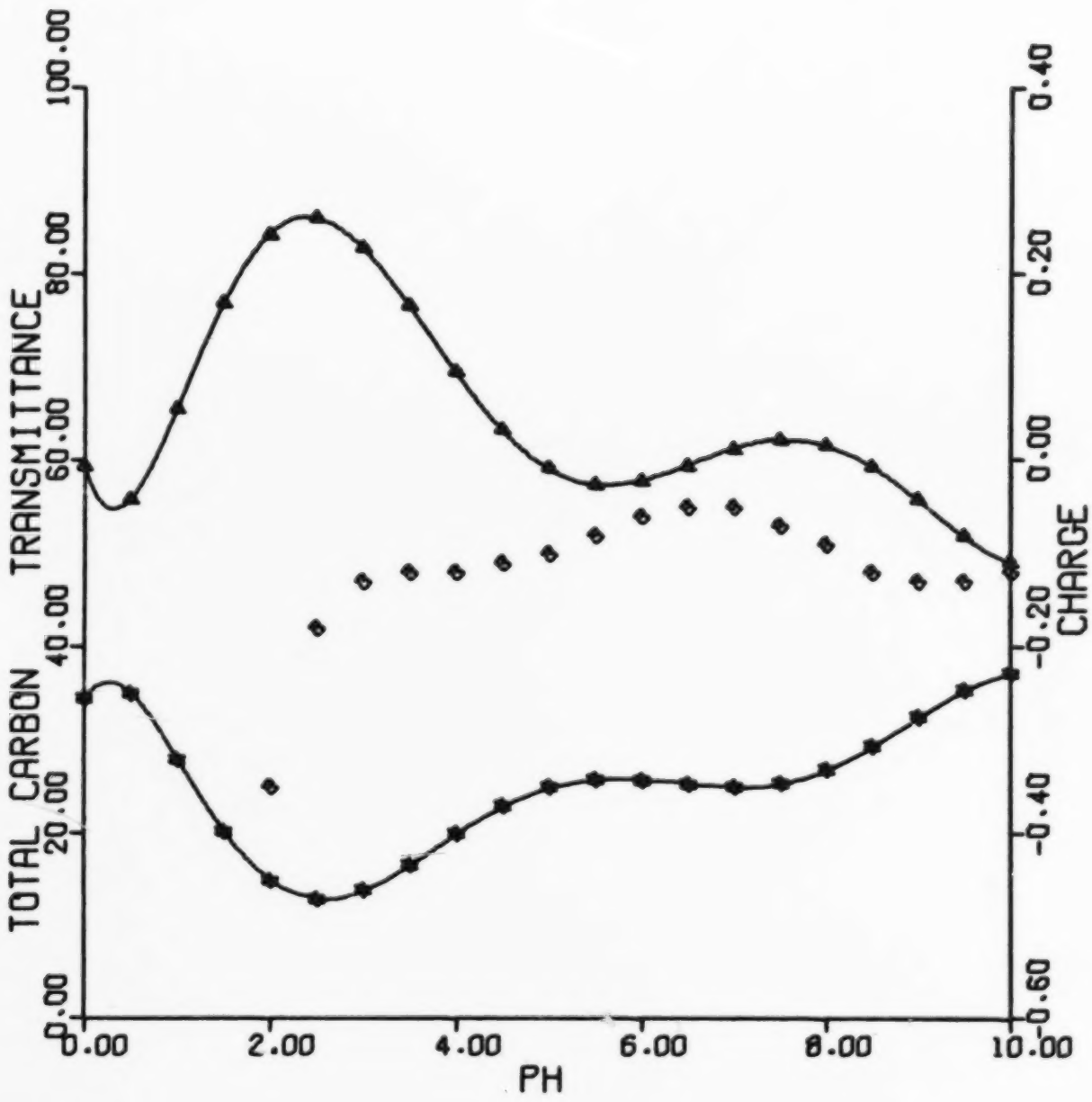


Figure 28

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 40

CALCIUM 0

MAGNESIUM 0

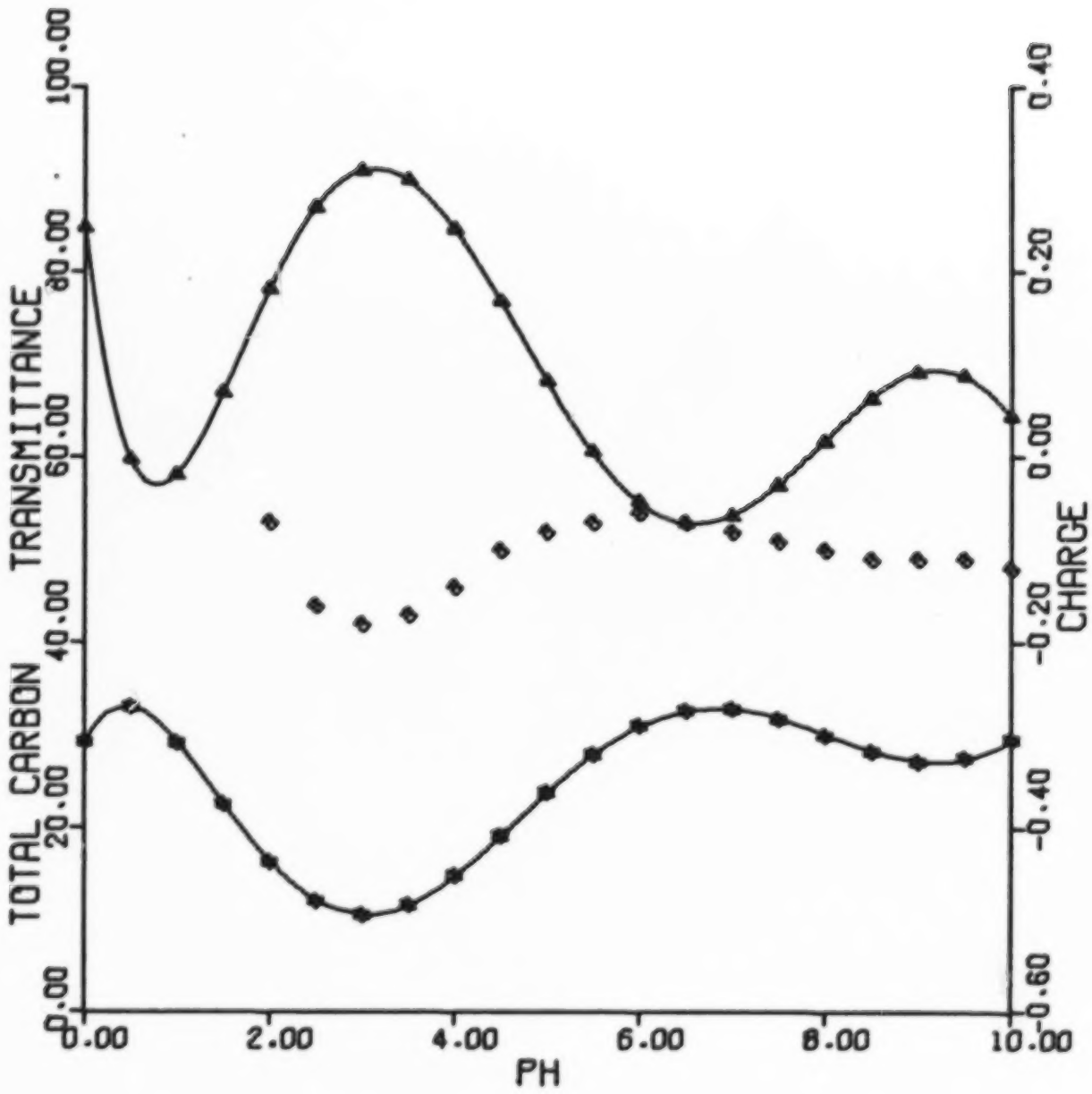


Figure 29

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 60

CALCIUM 0

MAGNESIUM 0

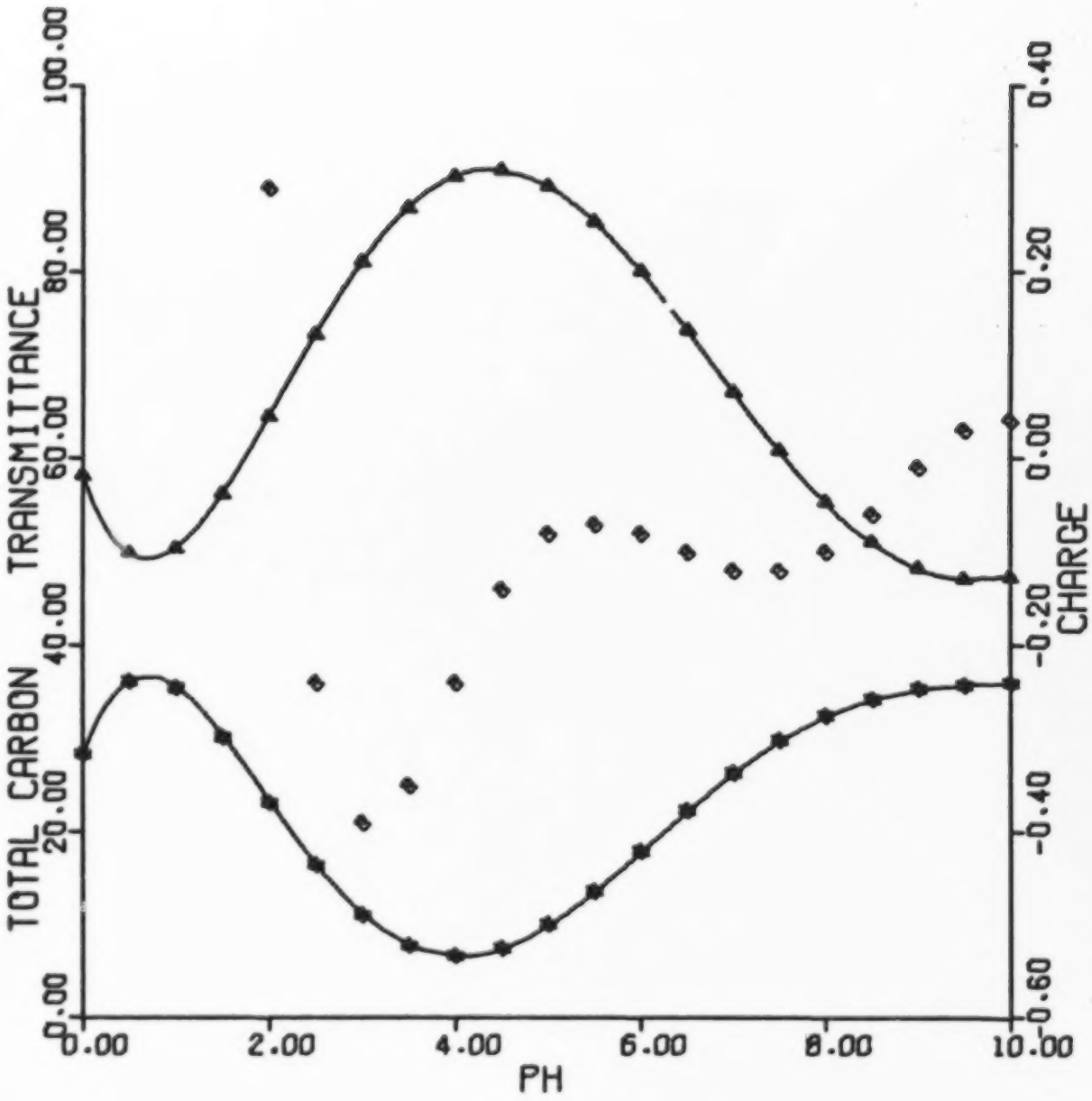


Figure 30

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 80

CALCIUM 0

MAGNESIUM 0

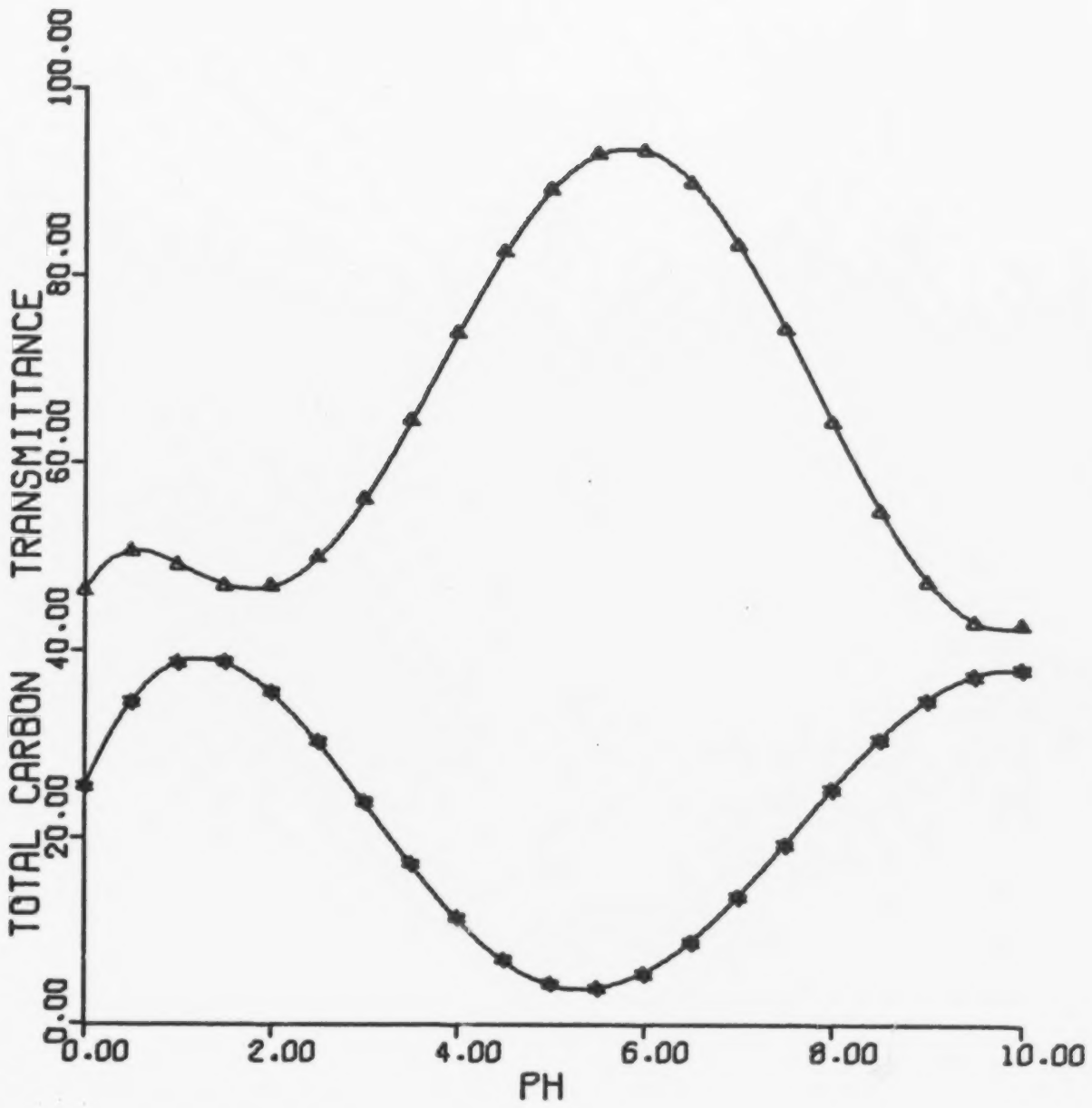


Figure 31

Δ Transmittance

* Total Carbon

THORIUM 100

CALCIUM 0

MAGNESIUM 0

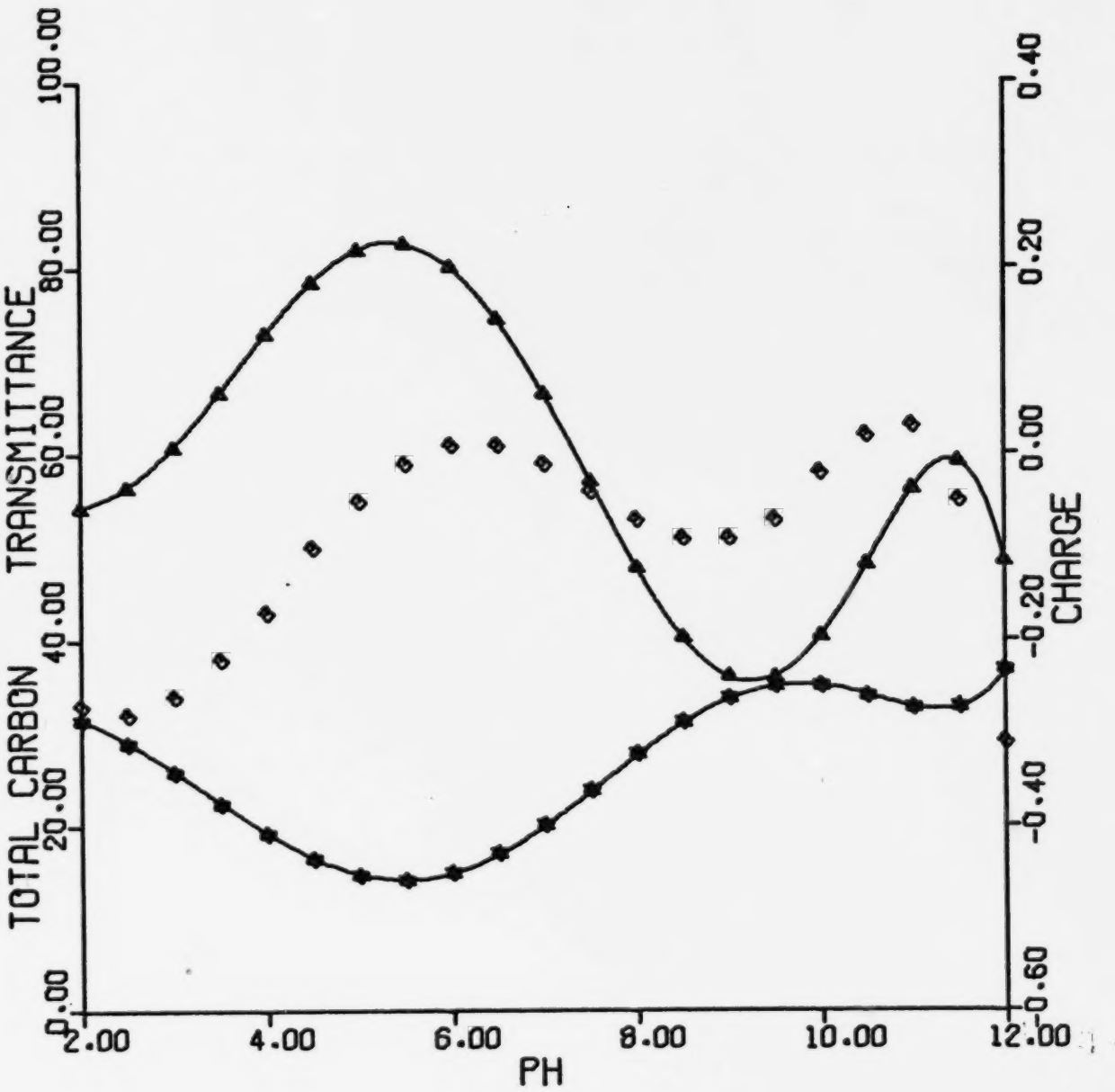


Figure 32

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 150

CALCIUM 0

MAGNESIUM 0

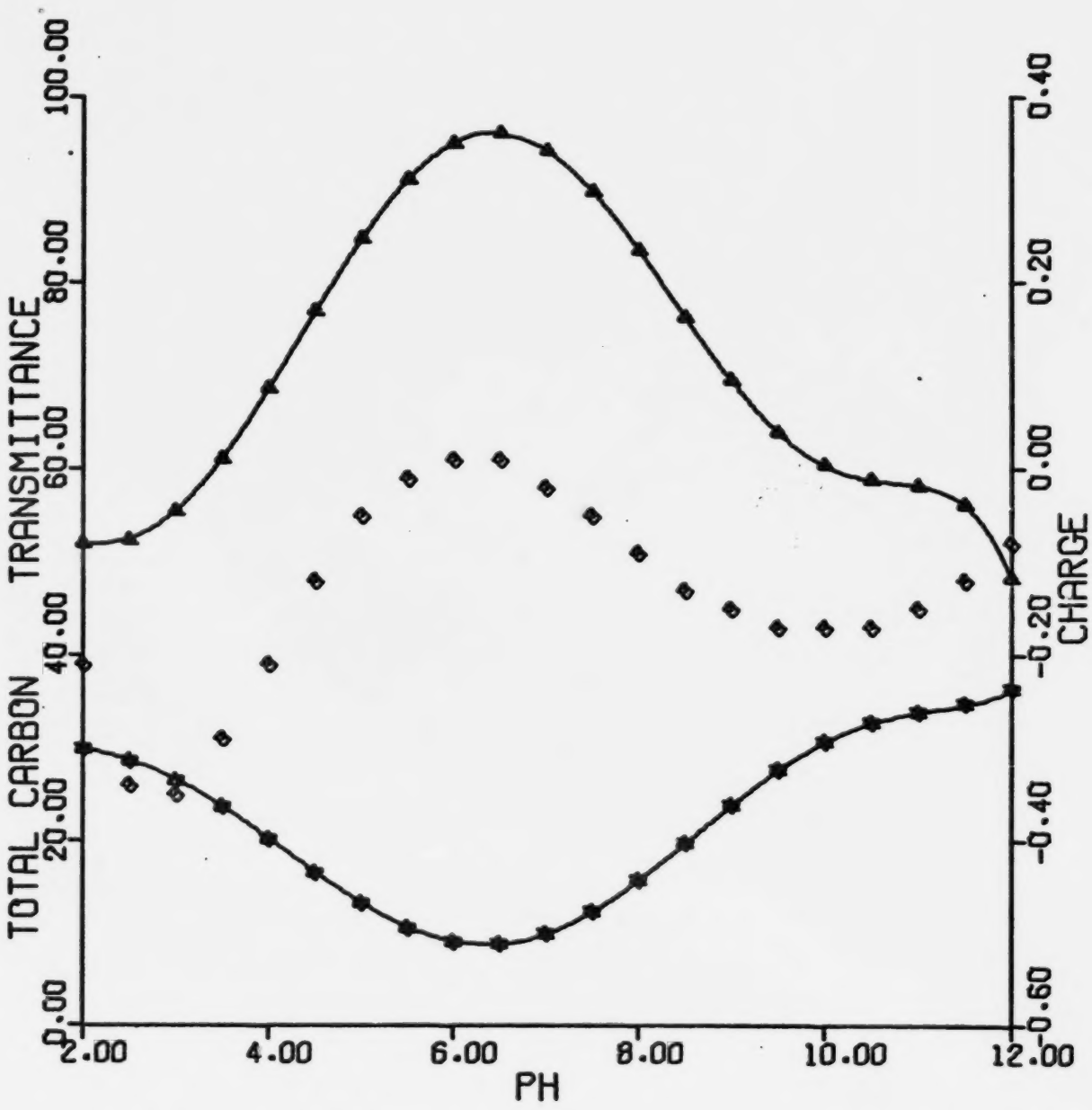


Figure 33

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 60

CALCIUM 18

MAGNESIUM 0

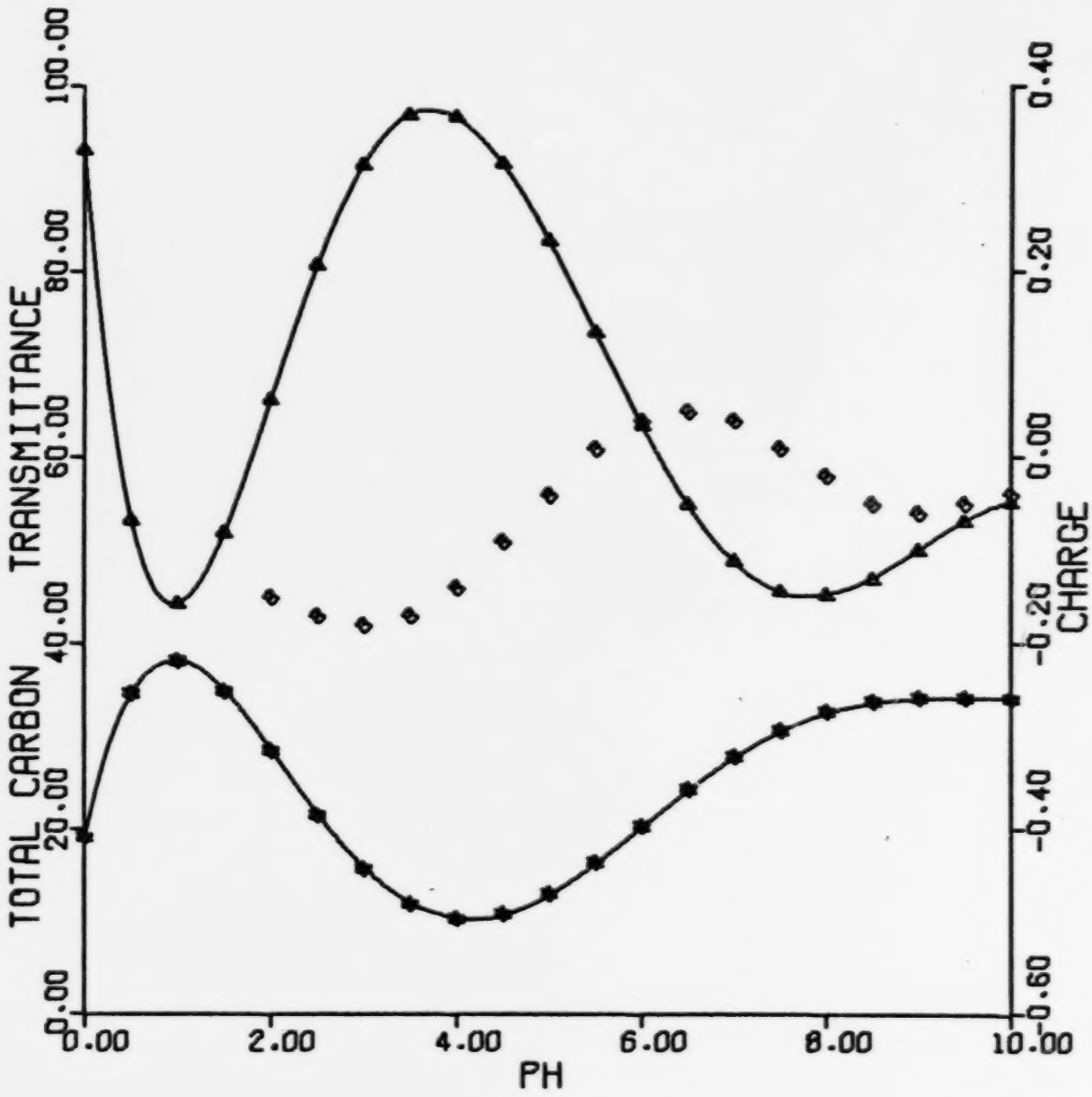


Figure 34

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 60

CALCIUM 37

MAGNESIUM 0

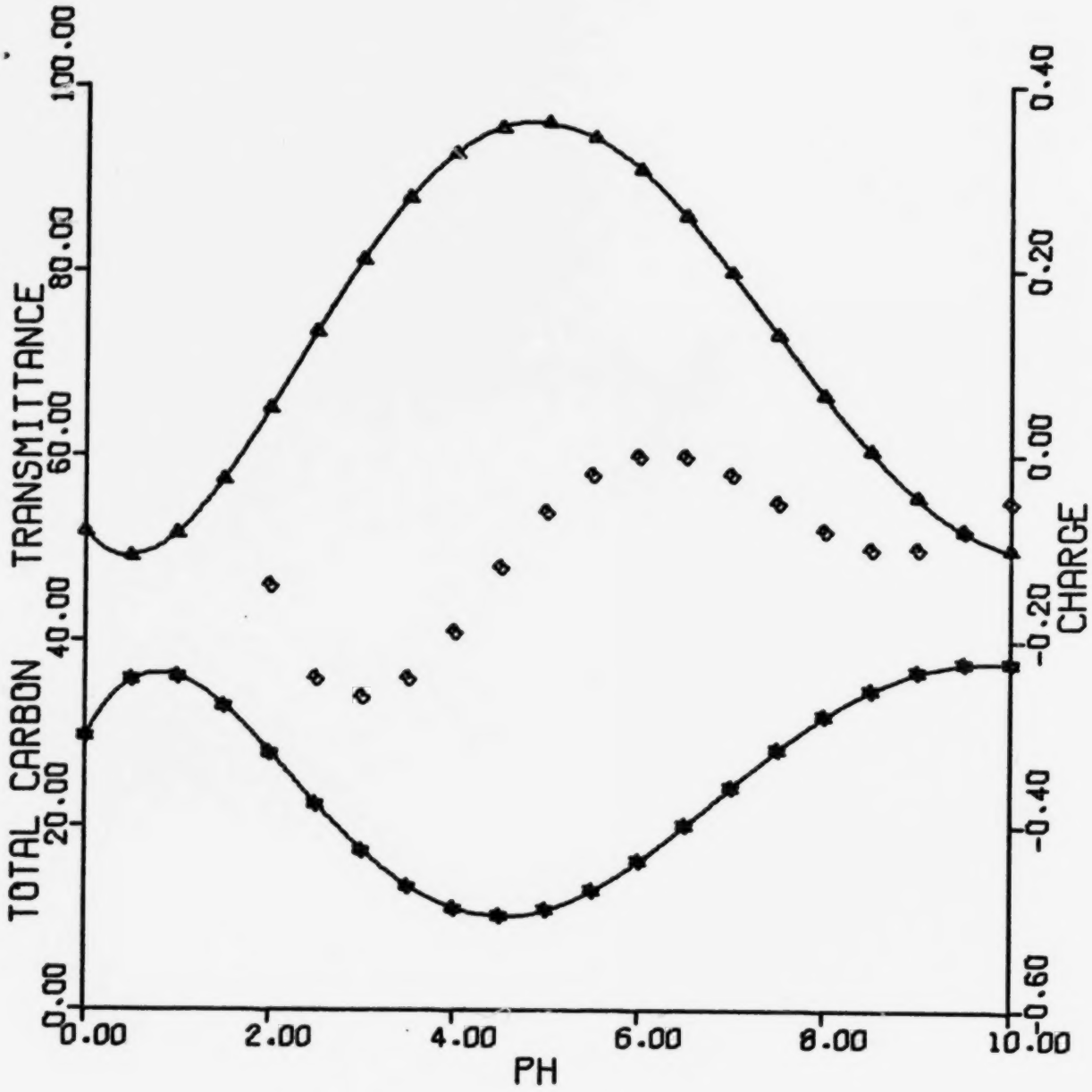


Figure 35

Δ Transmittance

■ Charge

* Total Carbon

THORIUM 40

CALCIUM 50

MAGNESIUM 0

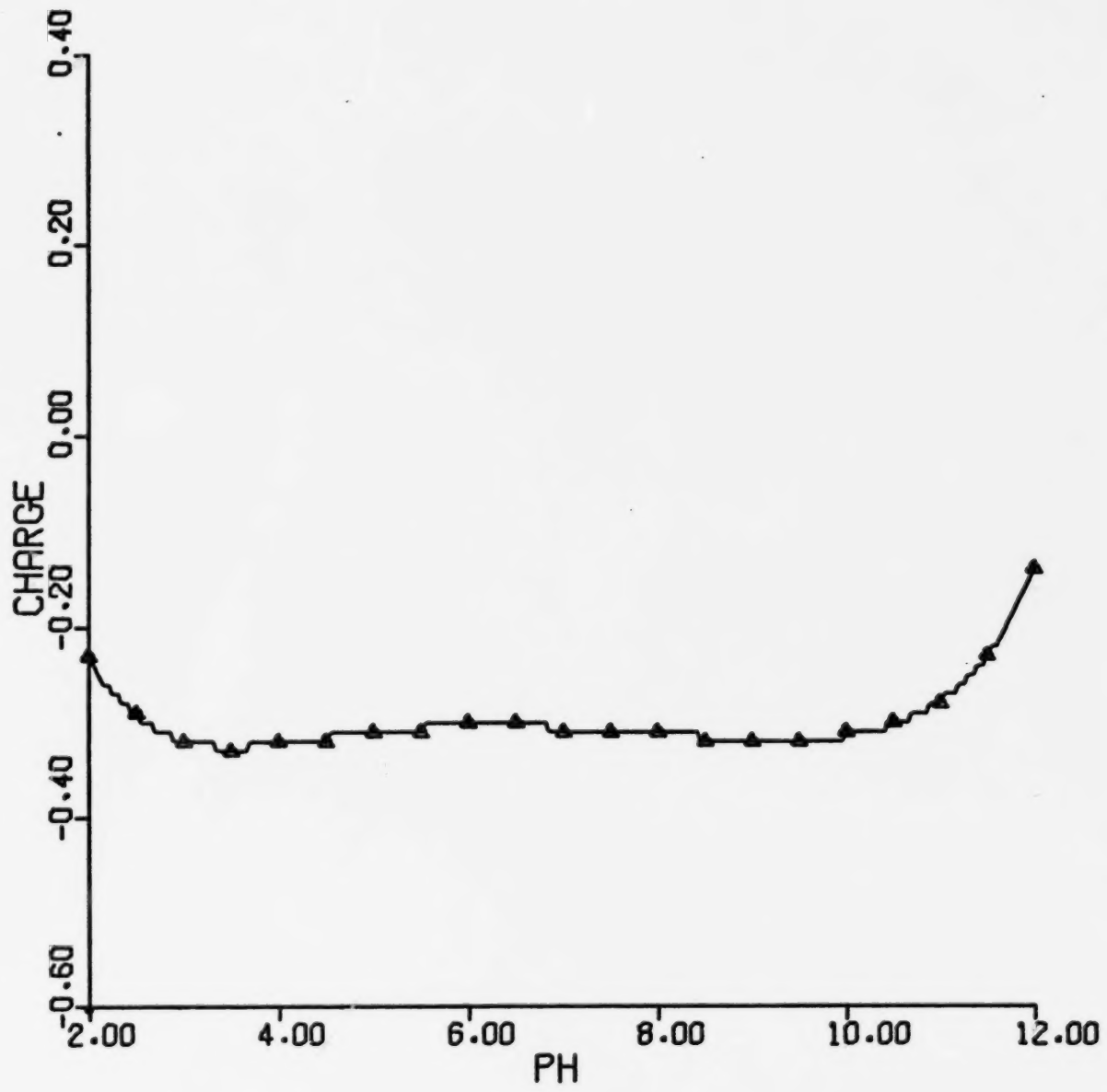


Figure 36

Δ Transmittance

THORIUM 40

CALCIUM 100

MAGNESIUM 0

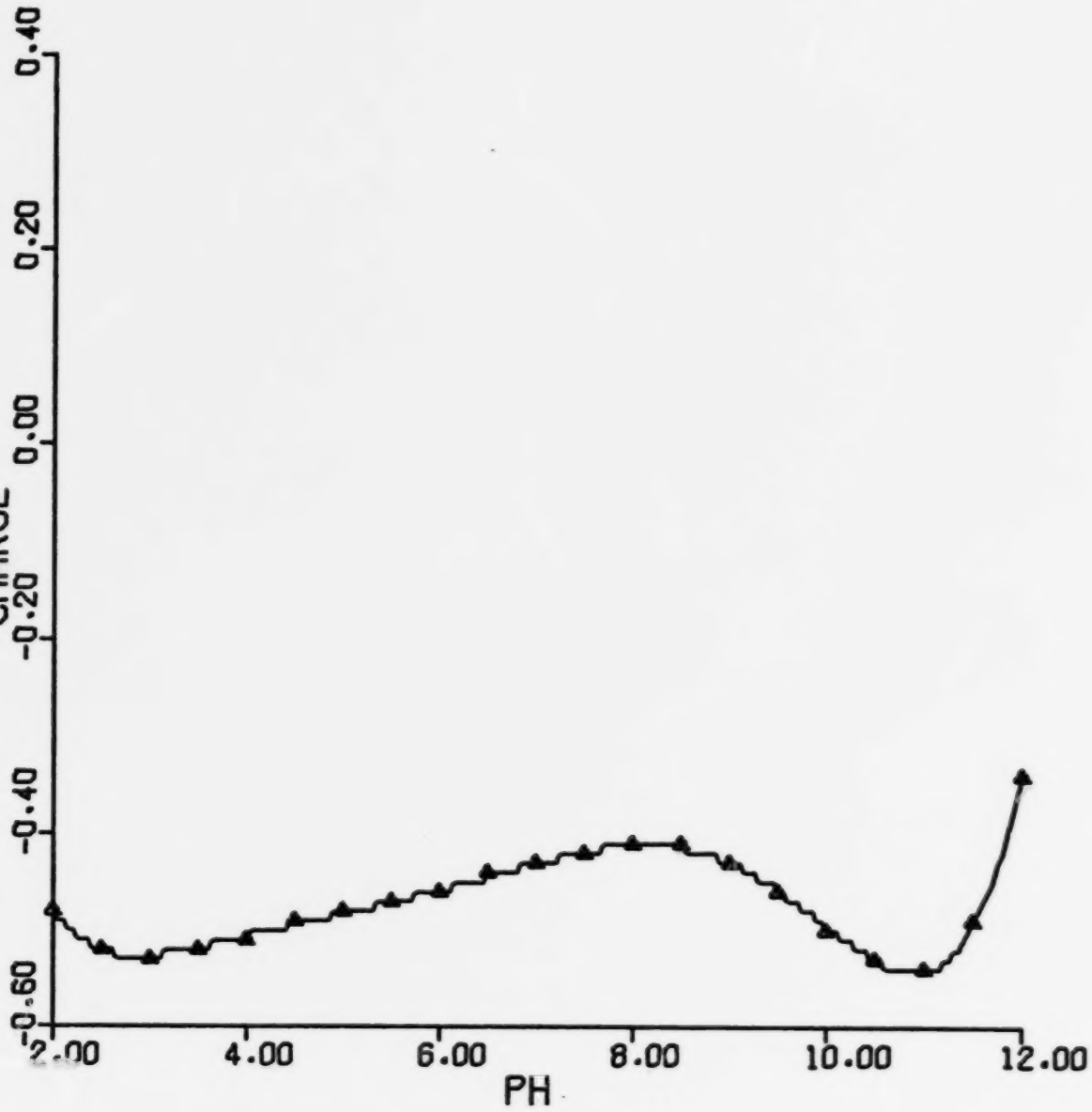


Figure 37

Δ Transmittance

LANTHANUM 0

ALUMINUM 0

THORIUM 0

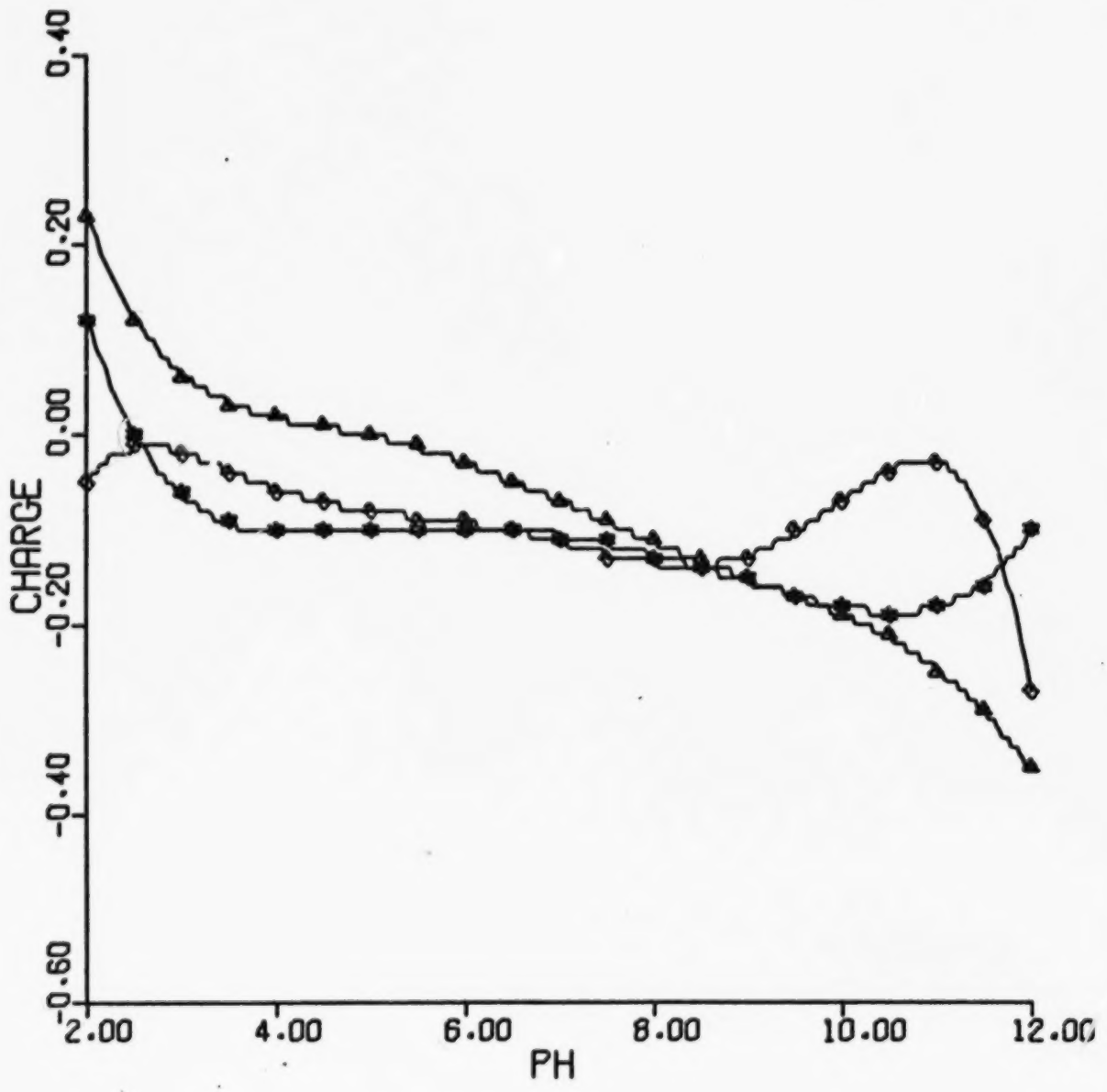


Figure 38

Δ Raw Water I

* Raw Water II

■ Raw Water III

LANTHANUM 0

ALUMINUM 0

THORIUM 0

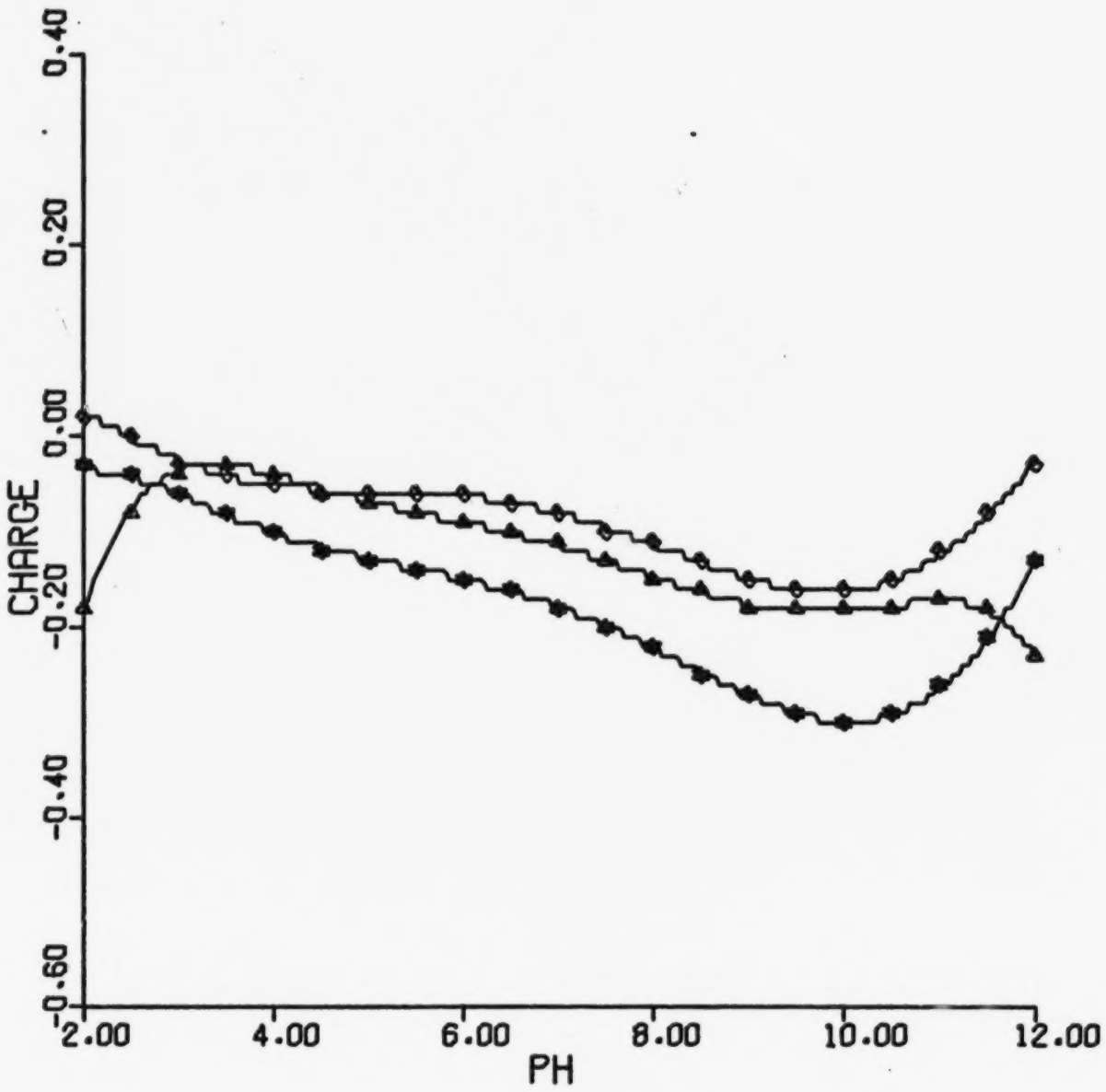


Figure 38 cont.

Δ Raw Water IV

* Raw Water V

■ Raw Water VI

ALUMINUM

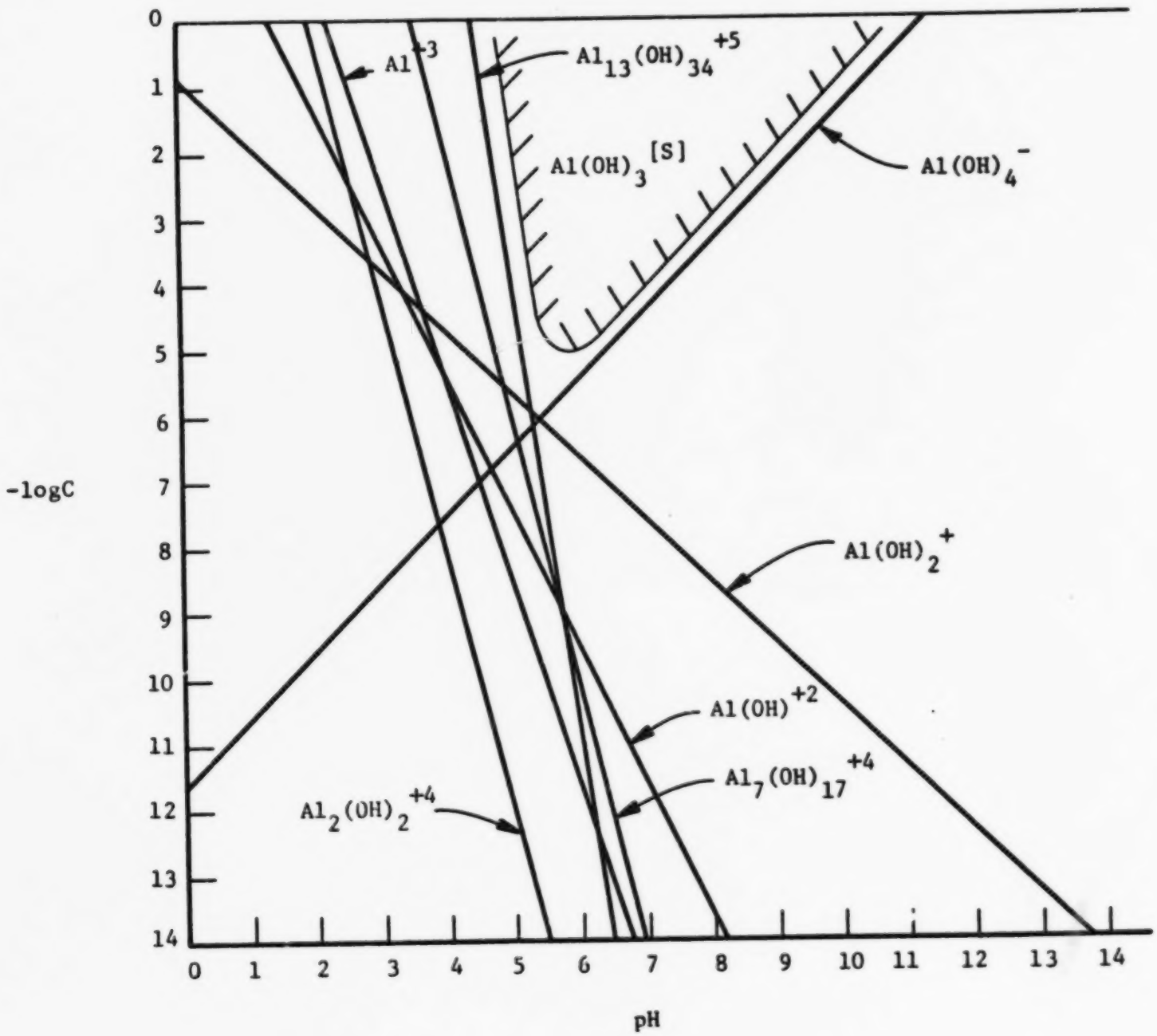


Figure 39

LANTHANUM

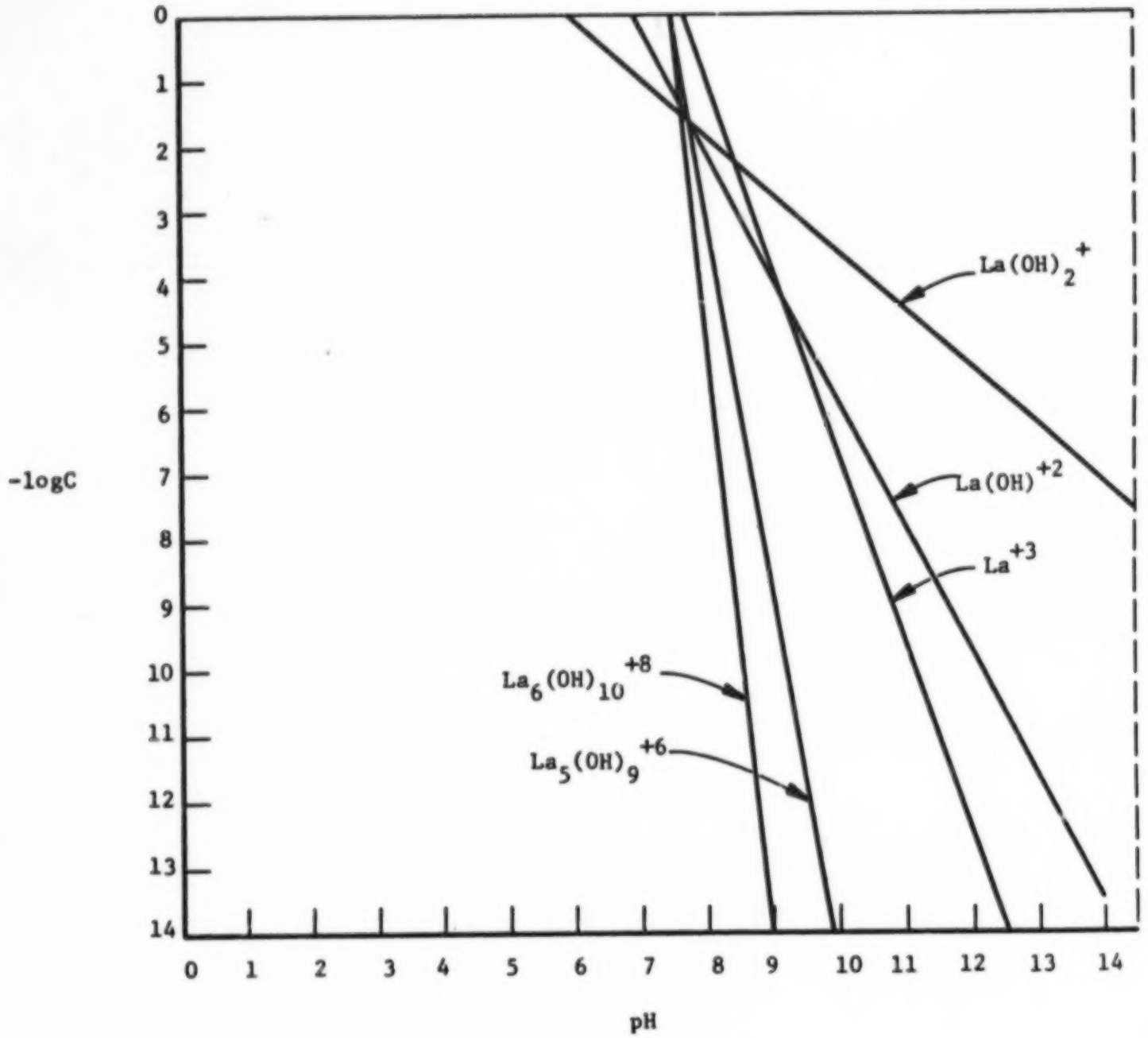


Figure 40

THORIUM

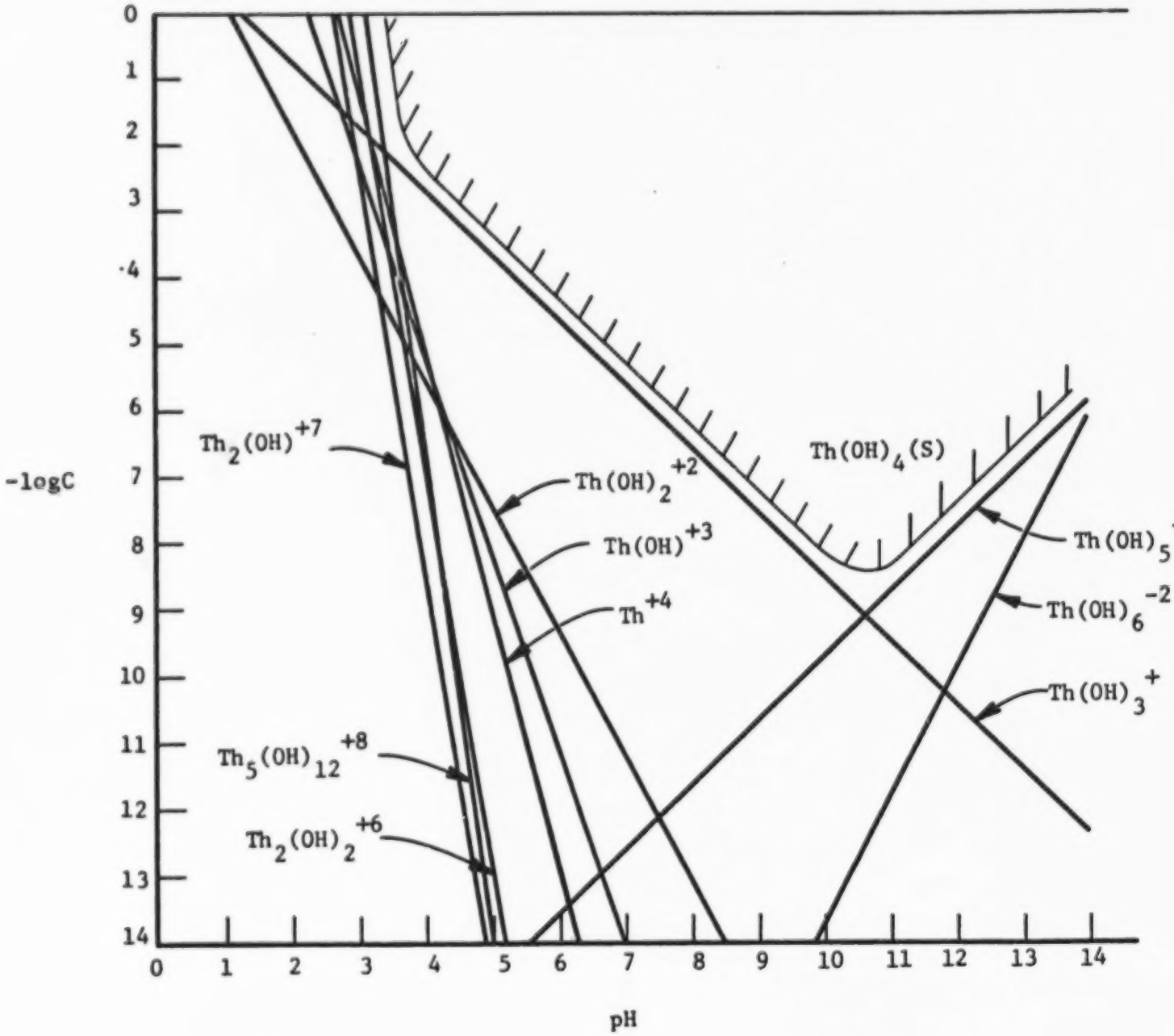


Figure 41

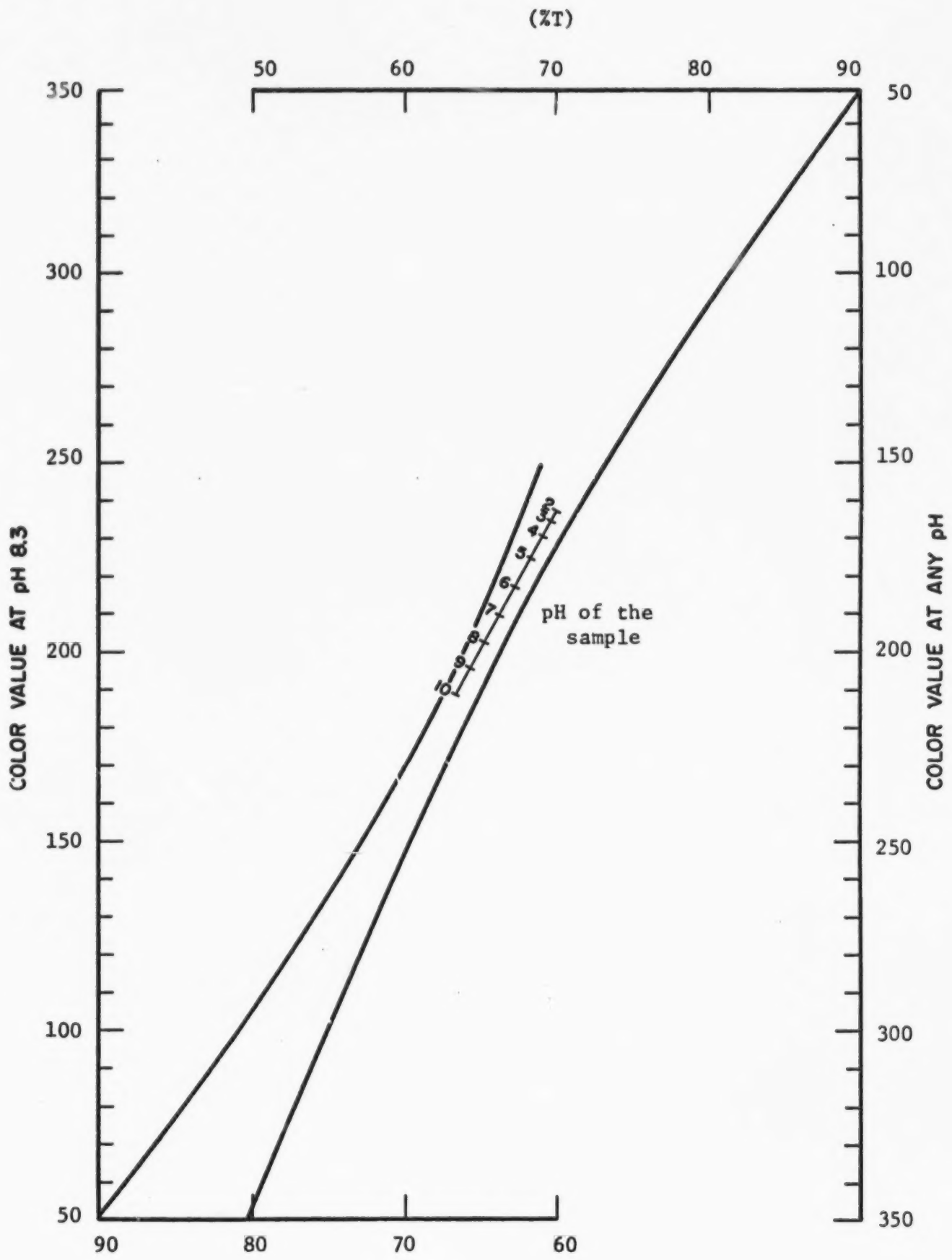

(%T)
50
60
70
80
90
350
300
250
200
150
100
50
COLOR VALUE AT pH 8.3
COLOR VALUE AT ANY pH
pH of the sample
1
2
3
4
5
6
7
8
9
10
90
80
70
60
(%T) @ pH 8.3

Figure 42

REFERENCES

1. Christman, R. F. and Arnquist, J. L. Fluorescence Techniques in Detection of Organics in Water. Microorganic Matter in Water, ASTM, STP 448, pp. 96-115 (1968).

2. Ghassemi, M. and Christman, R. F. Properties of the Yellow Organic Acids of Natural Waters. Limnology and Oceanography, Vol. 13, No. 4, pp. 583-597, October (1968).

3. Christman, R. F. Chemical Structures of Color Producing Organic Substances in Water. Symposium on Organic Matter in Natural Waters. Institute of Marine Science, University of Alaska, Fairbanks (Sept. 1968, In Press).

4. Pilipovich, J. B., Black, A. P., Eidsness, F. A., and Stearns, T. W. Electrophoretic Studies of Water Coagulation. Journal AWWA, 50:1467 (November 1958).

5. Black, A. P. and Williams, G. G. Electrophoretic Studies of Coagulation Removal of Organic Color. Journal AWWA, 53:589 (May 1961).

6. Black, A. P. and Christman, R. F. Chemical Characteristics of Fulvic Acids. Journal AWWA, 55:897 (July 1963).

7. Black, A. P., Singley, J. E., Whittle, G. P., and Maulding, J. S. Stoichiometry of the Coagulation of Color-Causing Organic Compounds with Ferric Sulfate. Journal AWWA, 55:1347 (October 1963).

8. Hall, E. S. and Packham, R. F. Coagulation of Organic Color with Hydrolyzing Coagulants. Journal AWWA, 57:1149 (September 1965).

9. Maulding, J. S. and Harris, R. H. Effect of Ionic Environment and Temperature on the Coagulation of Color-Causing Organic Compounds With Ferric Sulfate. Journal AWWA, 60:460 (April 1968).

10. Senju, R. Colloid Titration. Translation by M. Nakamura, University of Hokkaido, Sapporo, Japan (1970).

11. Kawamura, S. and Tanaka, Y. Applying Colloid Titration Techniques to Coagulant Dosage Control. Water & Sewage Works, 348 (1966).

12. Kawamura, S. Removal of Color by Alum Coagulation. Parts 1 and 2. Water and Sewage Works, Vol. 114, No. 8 and 9, August and September (1967).

13. Coagulation and Color Problems. Joint Report of Research Committee on Coagulation and Research Committee on Color Problems (AWWA). Journal American Water Works Association, Vol. 62, No. 5, pp. 311-314 (May 1970).

14. Stumm, W. and O'Melia, C. R. Stoichiometry of Coagulation. Journal AWWA, 60:514 (May, 1968).

15. Emery, R. M., Welch, E. B. and Christman, R. F. The Total Carbon Analyzer and Its Application to Water Research. Presented at the 36th Annual Meeting of the Pacific Northwest Pollution Control Association. November 5, 6 and 7, 1969, Seattle, Washington.

(in any order, in any manner as long as they all stay within 70 columns.)

b) from column 71 to 80

The number of mili-liter above which you want the plot for sample and blank titration to be started. (In other words the minimum value to be shown in the plot-out of the titration curves.) A range of 3 ml is used in this program. Statement No. 74 controls this range.

2. Sample titration data cards (in case of 30 sets of data)

a) first 10 cards

Each card takes three sets of pH - titration value data. The first thirty columns are to be used for pH values and the next thirty columns are to be used for titration values. The last twenty columns are not used at all. The figures should be punched in the same manner for pH and titration values. That is, every figure should be so punched that the decimal point comes to the sixth column of each interval (10 columns). See below. (F 10.4 FORMAT)

Original Data

pH	titration value
3.15	3.90
6.50	6.80
7.30	7.20

Punched card